

Arson Analysis Newsletter

CONTENTS

PAGE

"A Sensitive, Rapid
& Economical Method
for Analyzing Fire
Debris Using
Adsorption Elution
Techniques" 1

By: John A. Juhala
Frances K. Beever

"Impurities in
Activated
Charcoal" 13

By: Dr. Richard Henderson

NOTES 20

January 1986
VOLUME 9
NUMBER 1

ARSON ANALYSIS NEWSLETTER (AAN)

Published quarterly by S.E.A., Inc. (Systems Engineering Associates). The AAN is available for a subscription price of \$12.00 per year for subscribers within the United States and \$25.00 per year for subscribers outside of the United States. Back issues are available for purchase upon request.

Send all subscriptions and manuscripts to:

S.E.A., Inc.
Attn: Ronald N. Thaman
7349 Worthington-Galena Road
Columbus, Ohio 43085

The AAN solicits contributions from forensic scientists, arson investigators, attorneys, and interested parties who have some unique or routine analysis which helps in the identification of flammable liquid or explosive residues. Articles herein express the views and opinions of the authors and are not necessarily the views of the AAN or S.E.A., Inc.

EDITOR

Ronald N. Thaman, Manager-Corporate Laboratories
S.E.A., Inc., Columbus, Ohio.

ANY REPUBLICATION OF THE ARSON ANALYSIS NEWSLETTER (AAN) WITHOUT THE EXPRESS WRITTEN PERMISSION OF THE EDITOR OF THE AAN IS STRICTLY PROHIBITED.

Copyright © 1986 by S.E.A., Inc.

A SENSITIVE, RAPID AND ECONOMICAL METHOD FOR ANALYZING
FIRE DEBRIS USING ADSORPTION ELUTION TECHNIQUES.

John A. Juhala and Frances K. Beever

Michigan State Police
Bridgeport Crime Laboratory
P.O. Box H
Bridgeport, MI 48722

The analysis of fire debris today is frequently carried out using some form of sample concentration on charcoal or a porous polymer, followed by elution using a solvent or heat, with headspace analysis remaining as a rapid screening technique or in reserve for strong samples where the odor of a petroleum product is obvious. Adsorption on activated charcoal followed by elution with carbon disulfide is by far the most widely used technique although trapping the sample on a porous polymer such as Tenax GC followed by heat desorption has been used by several investigators and is a more sensitive technique because there is no dilution by a solvent (1,2). However, thermal desorption of porous polymers has not proved to be as popular as the charcoal purge and trap procedure for several reasons: The total sample collected is desorbed at one time and no second chance is available should there be a problem with the first run; very little automated equipment is available to handle this method; the actual desorption step is somewhat more cumbersome than a simple liquid injection and there are difficulties with trapping of very volatile hydrocarbons and alcohols. Its main advantages are sensitivity and the fact that no solvent is required for desorption.

Most of the charcoal adsorption methods use a relatively large quantity of charcoal, typically one to three inches in a disposable pipet, with elution carried out using a correspondingly large volume of solvent, 0.5 to 3 ml (3,4,5). The use of such large amounts of charcoal and solvent are unnecessary and introduce a tremendous dilution of the trapped hydrocarbons with a resulting loss of sensitivity. Of course the solvent can be readily concentrated by evaporation, but this is time consuming and also concentrates any impurities in the solvent or picked up elsewhere in the procedure. The large amount of charcoal also traps too much accelerant when a strong sample is encountered. This sometimes requires several reruns if a data system is not available on the gas chromatograph or else switching to an alternate technique such as headspace to deal with strong samples. A more desirable alternative is to adjust the sampling technique so that regardless of concentration all samples can be processed in the same fashion.

Experimental

Our goals were to minimize the dilution effects of using a solvent to elute the sample from charcoal, be simple to use, and allow for the use of an autosampler. We reported earlier on several procedures using small quantities of charcoal and carbon disulfide which had the requisite sensitivity, speed, and ease of implementation, however the coated bead produces a sample which contains too much charcoal dust for autosampling and the coated wire procedure uses such small volumes that it likewise cannot be used with an autosampler (6).

At the outset, the limiting factor was the requirement of the autosampler to have at least 50 ul of solvent to operate properly, according to the manufacturer. We elected to use 100 ul of carbon disulfide in a standard autosampler microvial (0.2 ml capacity). We quickly discovered that the Varian 8000 autosampler is not capable of controlling the pressure used to force the sample out of the vials to the syringe well enough to prevent all of the sample being expelled during the wash cycle. We then installed a second stage of regulation in series with the first using a capillary column pressure regulator. This provided a more even pressurization of the sample vials and offered some hope the autosampler could work with small volumes of carbon disulfide.

To trap the sample we use a disposable hypodermic needle, 18 gauge x 1½", which contains the charcoal in the hub. A very small amount of cotton is placed into the hub to prevent any of the charcoal from falling into the needle and plugging it. This is followed by approximately 6 mg of 50-200 mesh charcoal (Fisher Scientific) and another small plug of cotton. If done carefully there is still enough space left in the hub to allow the charcoal packed needle to be placed onto a standard luer-lock fitting which is then attached to any convenient vacuum source (see Figure 1). If needles with aluminum hubs are used a quantity can be packed ahead of time and stored for later use. Those with polyethylene hubs seem to contribute some artifacts which may increase with storage time. We are currently investigating the length of time the charcoal can remain in a polyethylene hub without picking up an objectional background.

To sample a polymer bag containing arson debris, the needle is merely pushed into the bag and sealed by clamping a forceps, which has a small hole drilled through the jaws, around the bag and needle. The container, which has been previously heated to 90°C, is then evacuated for a minute or two depending upon its size. With any type of rigid debris container two holes are first punched through the lid and then a packed needle which has been pushed through a standard G.C. septum is placed into one hole and a charcoal trap, either a second packed needle or a charcoal packed pasture pipet, is placed into the other hole. The septa provide a very good seal against the container lid and frequently the container will collapse even with an air inlet. We are currently using a small vacuum pump to evacuate the containers, but a water aspirator works equally well. After sampling, the needles are placed back into previously labeled 12 x 75 mm culture tubes and sealed with corks.

Elution of samples is carried out in a fume hood. The needles are placed into holes in a piece of cardboard. The holes are spaced to match those in a wooden block which holds 14 microvials. Approximately 100 ul of carbon disulfide are added to each needle using a pipet. The effluent is collected in the vials which are sealed with teflon faced septa. A room air blank, collected and processed in the same way as the debris samples, is included with each case.

The process is quick and economical. A pint of carbon disulfide will last for six months and a pound of charcoal for years. There is no apparatus to clean and the small volume of carbon disulfide reduces the fire and toxic hazard of this chemical. Once the samples are adsorbed the needles can be stored conveniently in a stoppered tube and processed at a later time.

Results

Although autosampling using the above procedure should work very well, in practice there are several problems which have prevented us from using the autosampler on a routine basis. The sampling system in use by Varian and several other manufacturers requires pressurizing the sample vial to force the sample through a transfer tube and into the syringe for injection. In order to clean the syringe and transfer line between injections to prevent carryover of the previous sample the line is flushed with the current sample before injection. This works fine with 2 ml sample volumes, but with 100 μ l samples this cannot be carried out effectively without using up all the sample in the wash cycle leaving nothing to inject. The only alternative is to place a 2 ml wash vial containing carbon disulfide between each sample and use this to wash the system between injections. However, this cuts the sample capacity from the typical sixty vials to thirty and as several cases are being run consecutively the room air blanks from each one occupy more of the available sample space. Thus, a full carousel may only handle three to five cases. Secondly, in spite of the addition of a second pressure regulator to control vial pressure we have not been able to get the autosampler to process an entire carousel without emptying some of the vials which then requires reprocessing those samples. A third problem encountered with older data systems such as the Vista 401 is the lack of sufficient disk space for data storage. This is particularly true when using capillary columns. Because of the limited disk space, it is necessary to collect the data points at less than the most desirable rate. If data points are collected fast enough to capture narrow capillary peaks only a few chromatograms can be stored on a disk. If the data collection rate is decreased to save disk space frequent loss of peak maxima occurs and the peaks look as though they have been chopped off. A reasonable compromise will allow only twelve chromatograms to be stored per disk. Thus, both the amount of available data storage and the need for wash vials to prevent sample carryover combine to restrict the number of samples which can be processed automatically with this particular system. Even four or five cases at a time, however, would be useful if the problem of emptying the vials during the pressurizing step could be eliminated, but the system has not yet proved reliable when handling a volatile, low viscosity solvent like carbon disulfide in 100 μ l volumes.

As a result of these limitations we decided to try the larger sample vials, i.e. 2 ml, coupled with a larger amount of charcoal and carbon disulfide. This eliminated the problem of emptying the sample vials and the system worked very well. Experience, however, had lead us to believe that using larger amounts of solvent and charcoal would not be as sensitive as working with the scaled down technique we have developed so we decided to test the two procedures side by side.

Two identical sets of samples were prepared. One set consisted of two pieces of 3/4" plywood to each of which was added 5 μ l of gasoline before being sealed into a polymer bag. The second set contained two similar pieces of carpet to which had been added 5 μ l of fuel oil. These samples were also sealed into polymer bags. The four samples were heated for one hour at 90° C. After one hour, the vapors from one sample in each set were trapped using a charcoal packed needle and those from the other set trapped on a charcoal packed pipet. Those from the packed needles were processed as described above and the charcoal packed needles were eluted using 2 ml of solvent. The eluted samples were run on a Varian Vista 6000 GC/401 Data System equipped with a J & W Megabore column, DB-1, 15 meters. The flow rate was 15 ml/min of hydrogen. The temperature program included a 4 min hold at 50 C followed

by programming at 14°C/min to 225 C. The resulting chromatograms are shown in Figures 2 and 3. The upper chromatogram in Figure 2 is from the gasoline sample adsorbed on the charcoal packed pipet, while the lower one is from the gasoline sample adsorbed on the charcoal packed needle. Figure 3 shows a similar comparison between the fuel oil samples. All chromatograms were run at the same attenuation of the electrometer, 10-11 x 2. The chromatograms resulting from the charcoal packed pipets do not show the presence of any flammable liquids while those from the packed needles would have to be attenuated considerably to be brought back on scale. The increase in sensitivity obtained by working with small amounts of charcoal and carbon disulfide is obvious.

Another example of the sensitivity of the procedure occurred unexpectedly. In the middle of February a series of peaks appeared in our room air blanks which had not been observed before. Over a period of several weeks they became fairly intense (see Figure 4). We examined all aspects of our procedure and found the artifacts were present in the laboratory air and were not from the procedure in use. We also found that the contaminant was identical to a charcoal lighter fluid marketed by the A & P grocery chain. We were unable to locate the source of the contaminant for several days until, while running our new office copy machine which was installed in January, it was necessary to change the toner and dispersant. At that time we discovered this machine used a liquid toner and dispersant whereas our old machine used dry chemicals. Of course the liquid toners and dispersants are petroleum based and our problem appeared shortly after the introduction of the new machine. Examination of the toner and dispersant showed them to be the source of the contaminant (see Figures 5 & 6). We sampled the laboratory air throughout the building as well as several sheets of paper coming from the copy machine. The solvent background was distributed everywhere in the building and was also on the paper from the copy machine (see Figures 7-9). Our building has a forced air heating/cooling system with little makeup air and this, coupled with hand carrying machine copies around the building distributes the vapors throughout. This background contamination would not have been observed using charcoal packed pipets with 2 ml of carbon disulfide for elution, but with the increased sensitivity of the packed needle it was becoming a serious problem since the contaminant is a known flammable liquid which we occasionally find in fire debris samples. We have since replaced our copy machine with one using dry chemicals and the background is slowly disappearing.

Summary

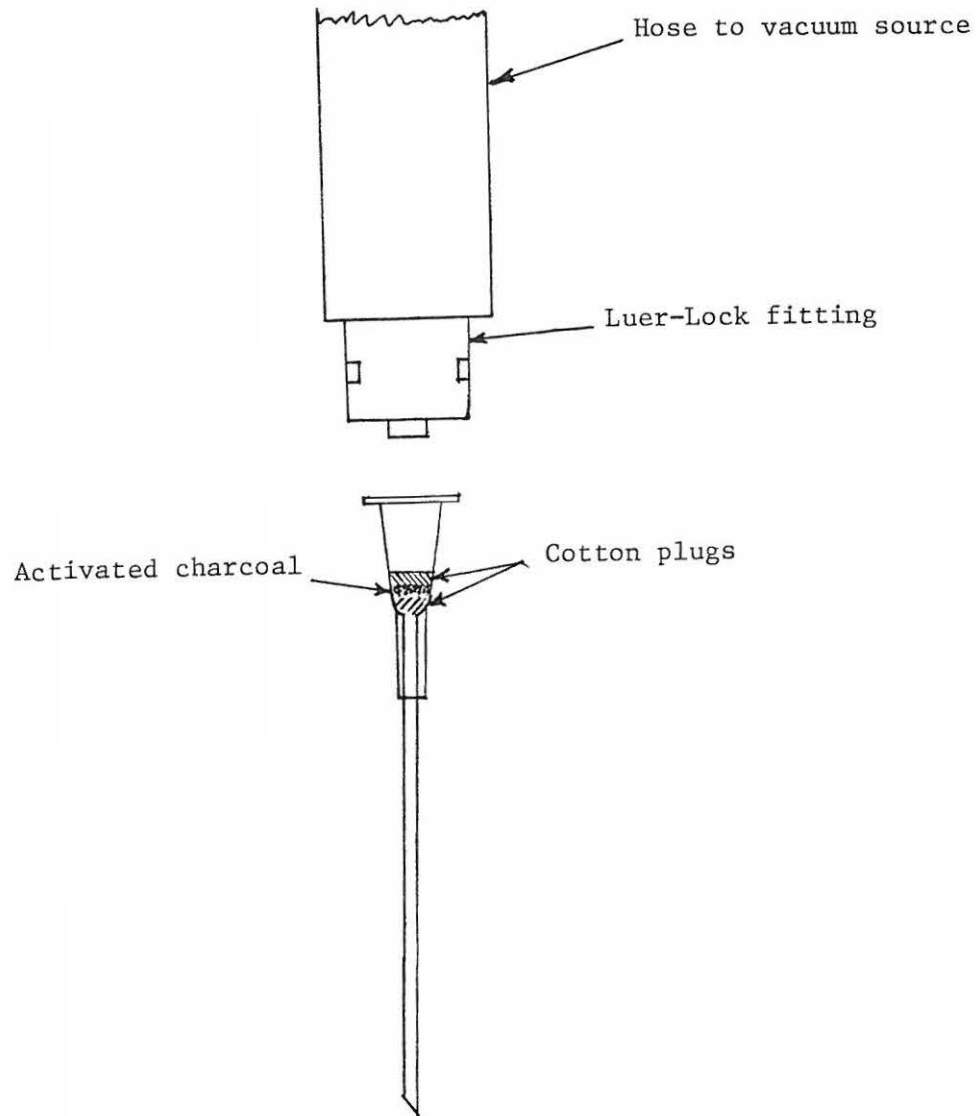
The examples described above show there are considerable benefits to be obtained by reducing the amount of charcoal and solvent when carrying out purge and trap procedures as is common in the analysis of arson debris samples today. It is possible to obtain a significant increase in sensitivity, speed of processing and reduce costs. The small volume samples have not yet proved amenable to our autosampler, but with a system such as the H-P which inserts the syringe directly into the sample and a data system with sufficient data storage it would be possible to process a large number of arson samples automatically with a minimum of attention by the analyst.

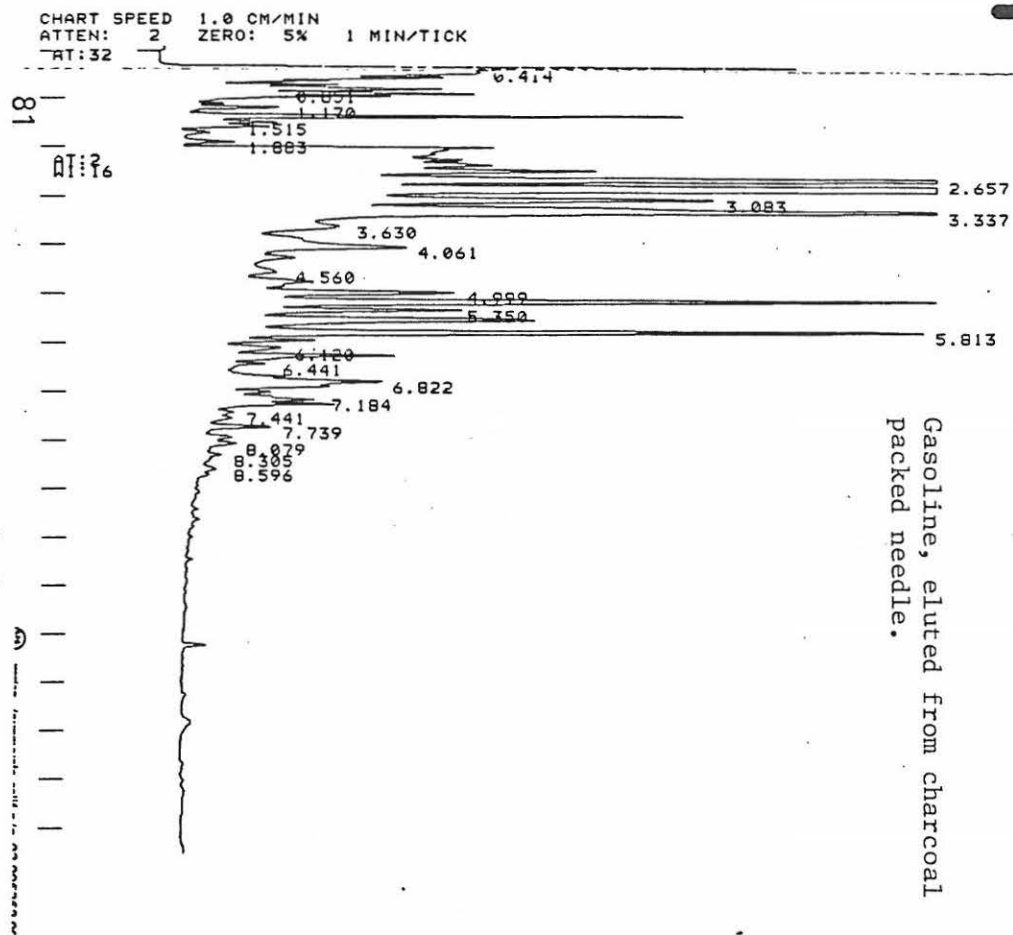
While we are currently looking at some of the parameters associated with the method such as equilibration time, solvent volume and efficiency of desorption, the procedure described has become our standard method of analysis for all arson samples whether neat liquids or debris. It is not necessary to switch from purge and trap for weak samples, to headspace for strong samples or screen with headspace and run negatives on purge and trap. The method allows cases to be batch processed with confidence that weak samples will not be missed and strong samples will not be outside the range of the electrometer and samples do not have to be segregated for special handling.

References

1. Russell, L.W.:The Concentration and Analysis of Volatile Hydrocarbons in Fire Debris Using Tenax-GC, J. Forens. Sci. Soc., 21, 317 (1981).
2. Saferstein, R. and Park, S. A.:Application of Dynamic Headspace Analysis to Laboratory and Field Arson Investigations, J. For. Sci., 27, 484(1982).
3. Chrostowski, J. W. and Holmes, R. M.:Collection and Determination of Accelerant Vapors from Arson Debris, AAN, 3, No. 5, 1 (1979).
4. Klosterman, J. P.:Simplified Technique for Charcoal Adsorption/Elution of Arson Samples, AAN,7, 26 (1983).
5. Levine, R. S., national Bureau of Standards, Private Communication (1981).
6. Juhala, J. A.:A Method for Adsorption of Flammable Vapors by Direct Insertion of Activated Charcoal into the Debris Samples., AAN, 6, 32 (1982).

Figure 1.





RECALC
TITLE: CHARCOAL TUBE/NEEDLE TEST

14:55 7 FEB 86

CHANNEL NO: 1 SAMPLE: GAS/NEED

METHOD: TEST

PEAK NO	PEAK NAME	RESULT ATTN	TIME (MIN)	TIME OFFSET	HEIGHT COUNTS	SEP CODE	W1/2 (SEC)
1		13.2470	0.414		13247	BV	15.90
2		9.4070	0.851		9407	VV	21.50
3		4.7270	1.170		4727	VV	6.00
4		20.6430	1.367		20643	VV	2.95
5		4.6900	1.515		4690	VV	9.90
6		3.0020	1.883		3002	VV	19.15

CHART SPEED 1.0 CM/MIN
ATTN: 2 ZERO: 5% 1 MIN/TICK
AT:32

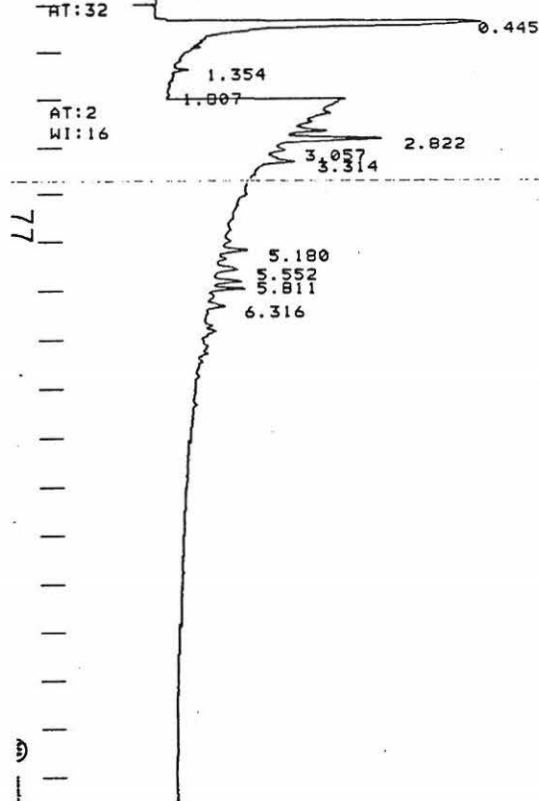


Figure 2.
Gasoline, eluted from charcoal
packed disposable pipet.

RECALC
TITLE: CHARCOAL TUBE/NEEDLE TEST

13:30 7 FEB 86

CHANNEL NO: 1 SAMPLE: GAS/PIPE

METHOD: TEST

PEAK NO	PEAK NAME	RESULT ATTN	TIME (MIN)	TIME OFFSET	HEIGHT COUNTS	SEP CODE	W1/2 (SEC)
1		12.8320	0.445		12832	BV	7.85
2		1.2930	1.354		1293	VV	27.25
3		0.4490	1.807		449	VV	?
4		0.3050	2.209		305	VV	?
5		0.2850	2.655		285	VV	3.40
6		0.4050	2.822		405	VV	8.75
7		0.1560	3.057		156	VV	3.60
8		0.1620	3.314		162	VB	10.00

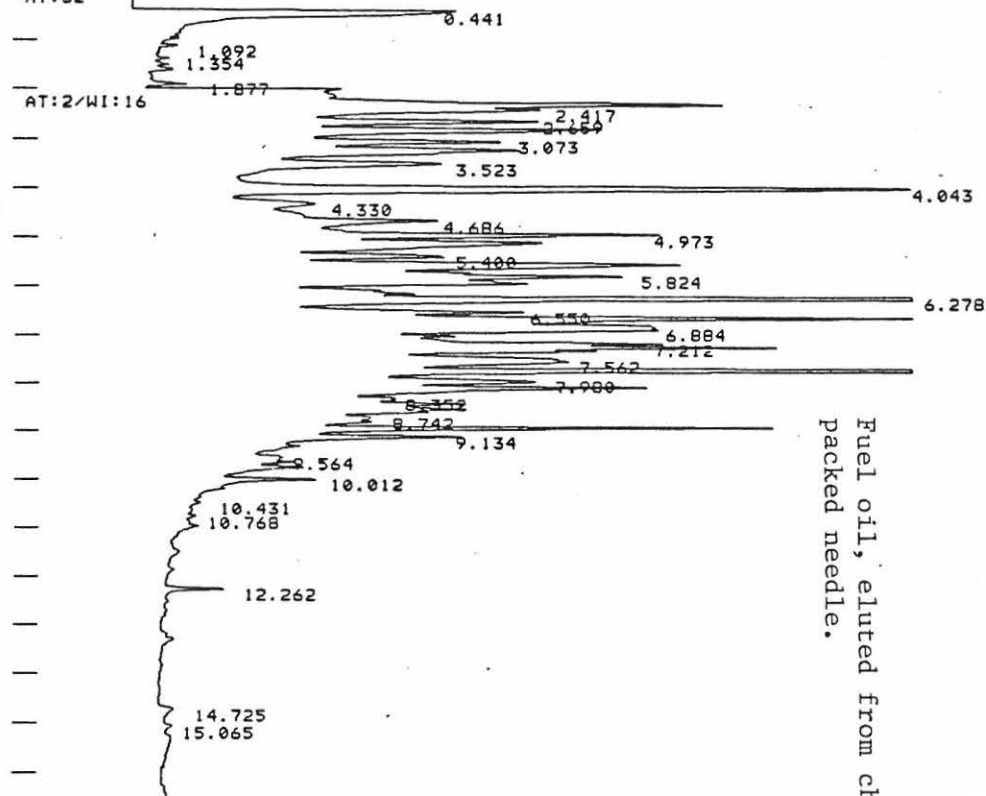
TOTALS: 15.8870

15887

DETECTED PKS: 14 REJECTED PKS: 6

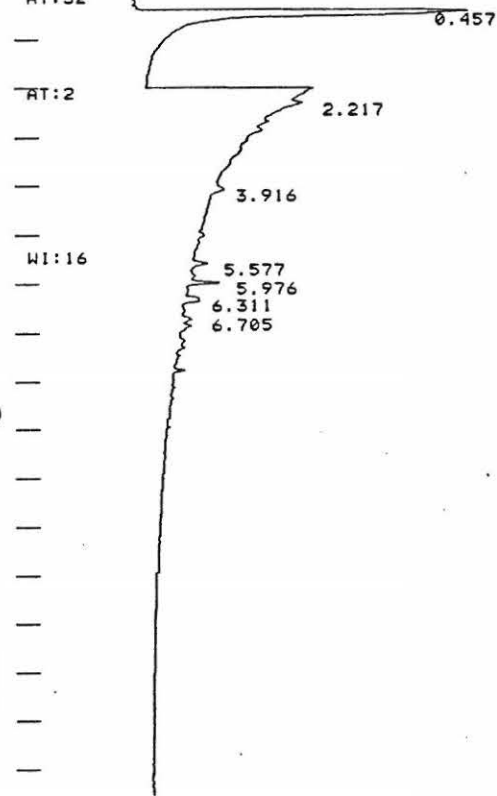
78

CHART SPEED 1.0 CM/MIN
ATTEN: 2 ZERO: 5% 1 MIN/TICK
AT:32



Fuel oil, eluted from charcoal
packed needle.

CHART SPEED 1.0 CM/MIN
ATTEN: 2 ZERO: 5% 1 MIN/TICK
AT:32



Fuel oil, eluted from charcoal
packed disposable pipet.

Figure 3.

RECALC
TITLE: CHARCOAL TUBE/NEEDLE TEST
CHANNEL NO: 1 SAMPLE: FUEL/NEED

14:29 7 FEB 86
METHOD: TEST

RECALC
TITLE: CHARCOAL TUBE/NEEDLE TEST
CHANNEL NO: 1 SAMPLE: FUEL/PIPE

13:58 7 FEB 86
METHOD: TEST

PEAK NO	PEAK NAME	RESULT ATTN	TIME (MIN)	TIME OFFSET	HEIGHT COUNTS	SEP CODE	W1/2 (SEC)
1		12.1220	0.457		12122	BV	8.20
TOTALS:		12.1220			12122		

CHART SPEED 1.0 CM/MIN
ATTEN: 1 ZERO: 5% 1 MIN/TICK
STAT: INJECT
AT: 32/WI: 1.0

0.425

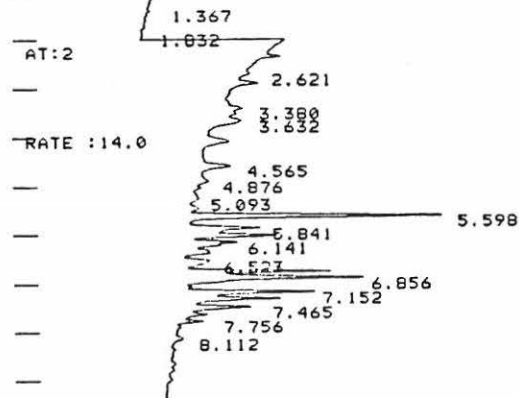


Figure 7.
Evidence Room
atmosphere

CHART SPEED 1.0 CM/MIN
ATTEN: 1 ZERO: 5% 1 MIN/TICK
AT: 128

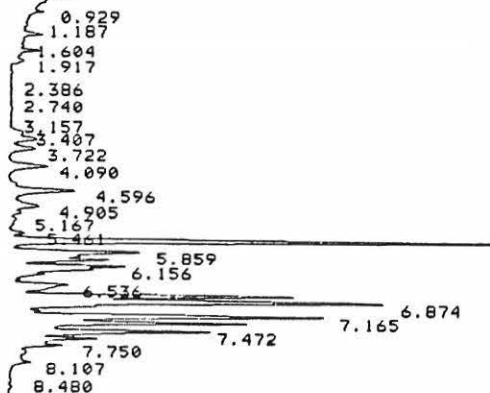


Figure 6.
Savin Dispersant

TITLE: COPY MACHINE ATM.NEEDLES
CHANNEL NO: 1 SAMPLE: EVID ROOM

15:41 19 FEB 86
METHOD: F

CHART SPEED 1.0 CM/MIN
ATTEN: 1 ZERO: 5% 1 MIN/TICK
STAT: INJECT
AT: 32/WI: 1.0

0.417

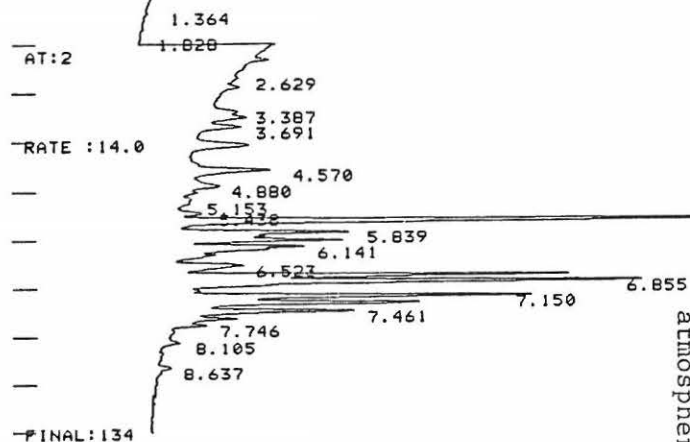


Figure 4.
Instrument room
atmosphere

RECALC
TITLE: COPY MACHINE ATM.NEEDLES
CHANNEL NO: 1 SAMPLE: SAVIN DISPER

13:47 19 FEB 86
METHOD: F

CHART SPEED 1.0 CM/MIN
ATTEN: 1 ZERO: 5% 1 MIN/TICK
AT: 128

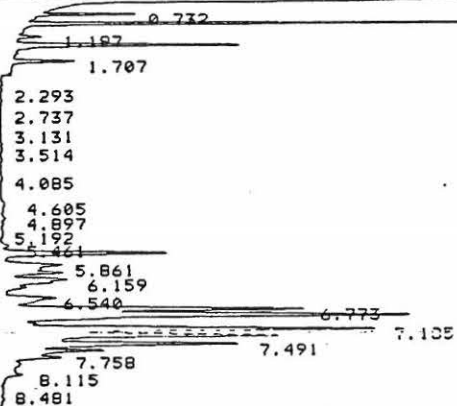


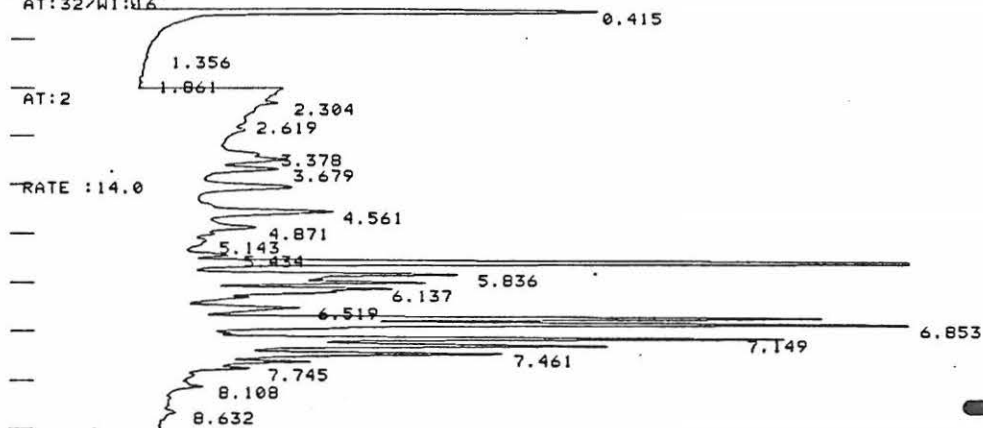
Figure 5.
Savin Toner.

12.254

03 00636200

CHART SPEED 1.0 CM/MIN
ATTEN: 1 ZERO: 5% 1 MIN/TICK

STAT: INJECT
AT: 32/WT: 0.8



Administrative office
atmosphere.

Figure 9.

TITLE: COPY MACHINE ATM.NEEDLES
CHANNEL NO: 1 SAMPLE: OFFICE

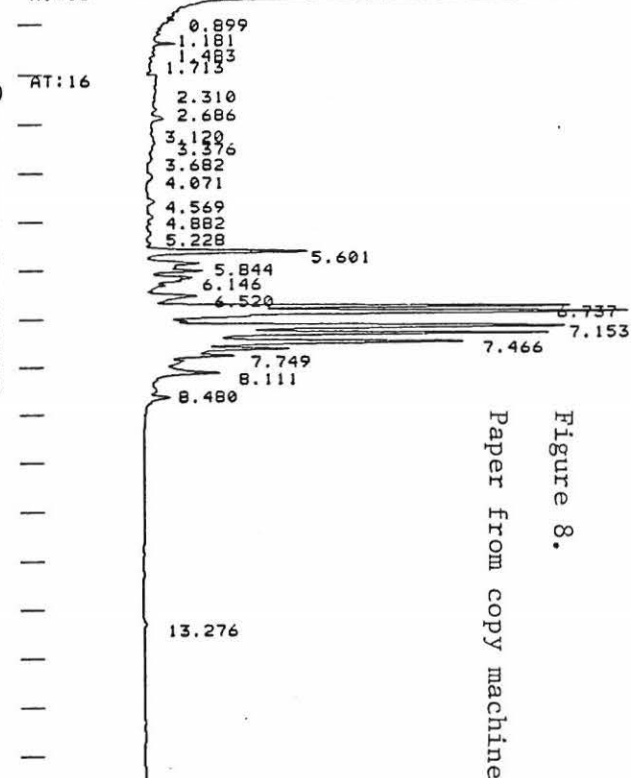
14:40 19 FEB 86
METHOD: F

- 11 -

185

CHART SPEED 1.0 CM/MIN
ATTEN: 1 ZERO: 5% 1 MIN/TICK

AT: 16



Paper from copy machine
Figure 8.

RECALC
TITLE: COPY MACHINE ATM.NEEDLES

CHANNEL NO: 1 SAMPLE: PRINTEDPAPER

12:49
METHOD: F

180

IMPURITIES IN ACTIVATED CHARCOAL

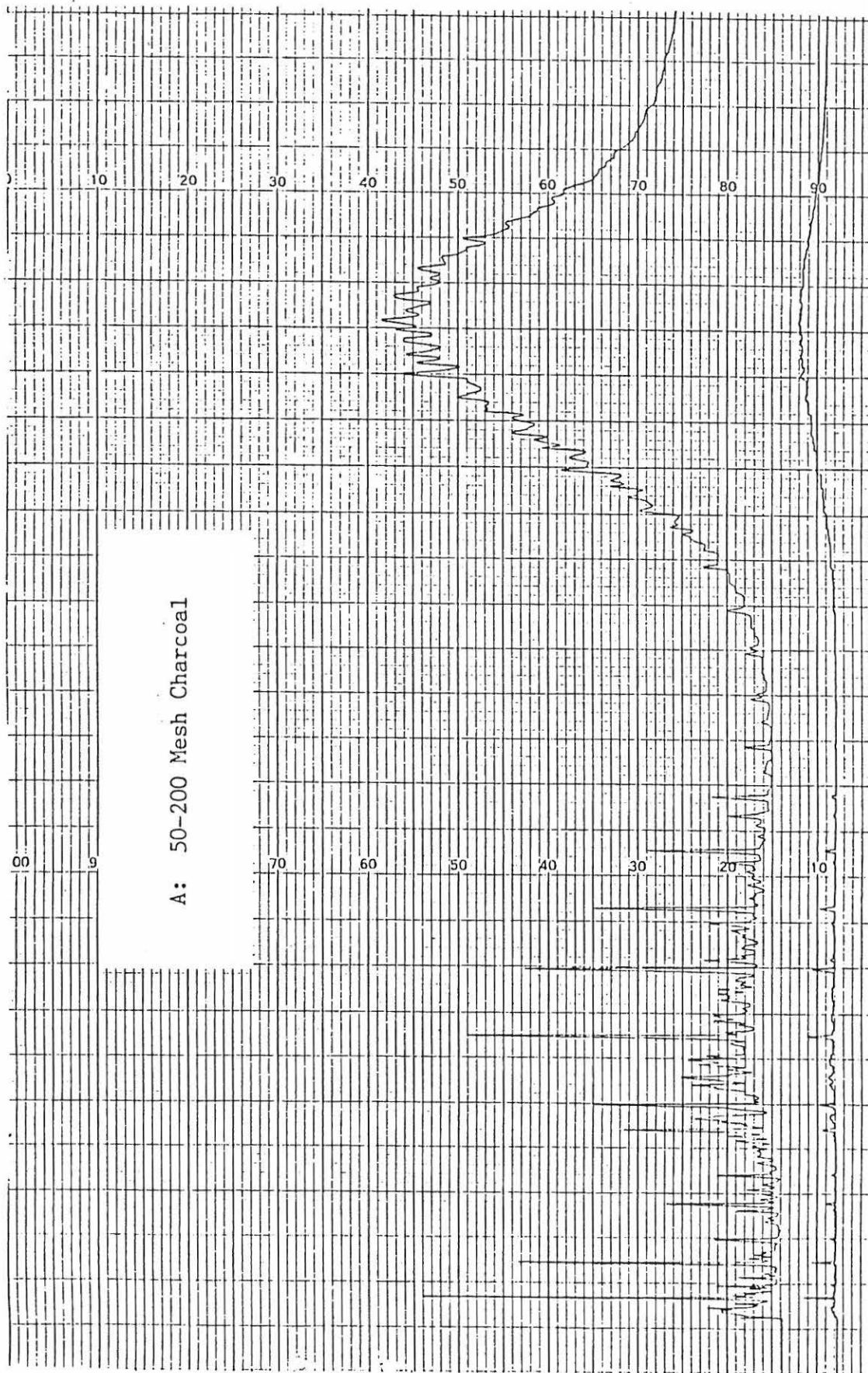
By

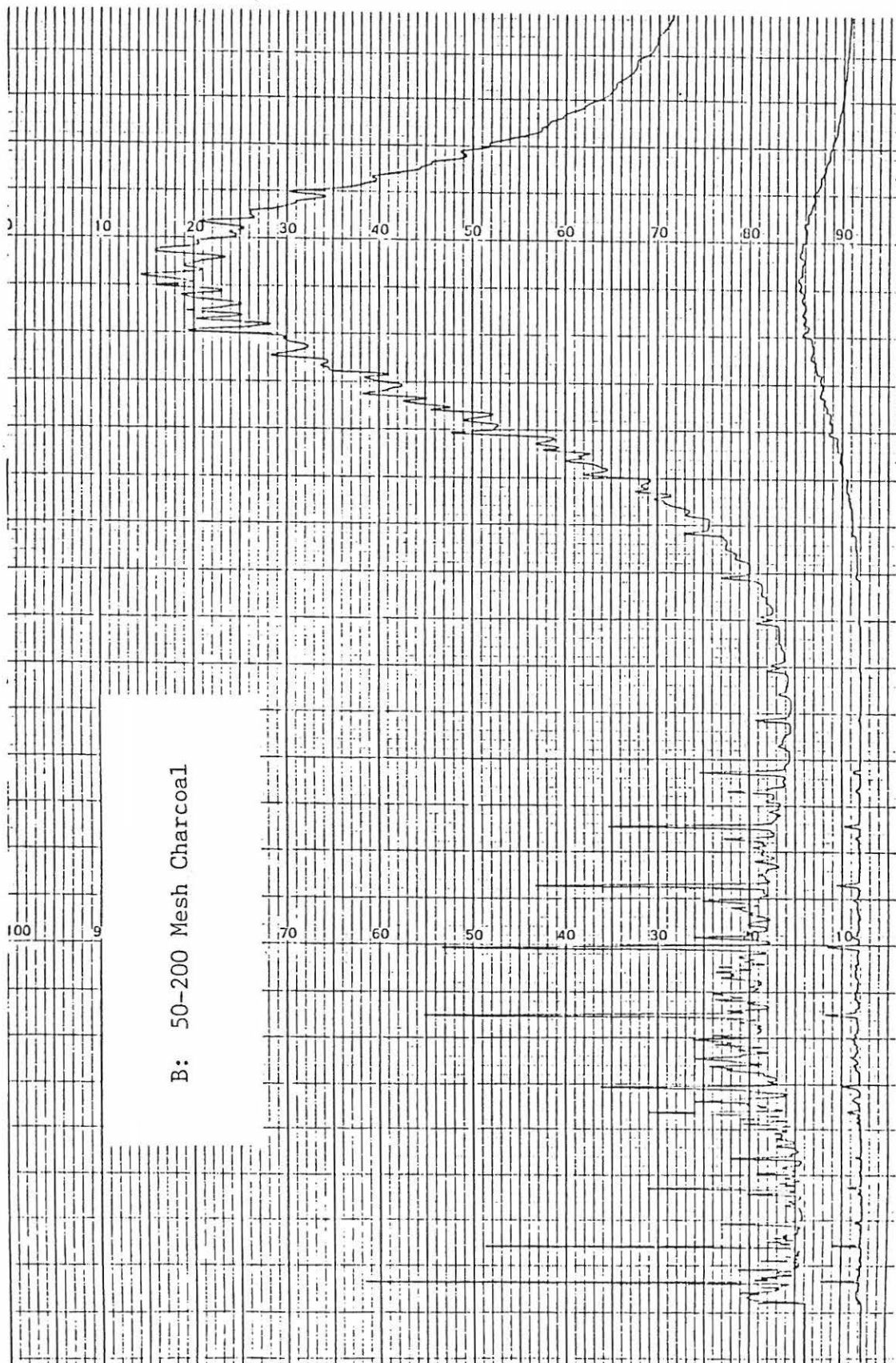
Dr. Richard W. Henderson
Southeastern Research Laboratories, Inc.
P.O. Box 15120
Quinby, SC 29501

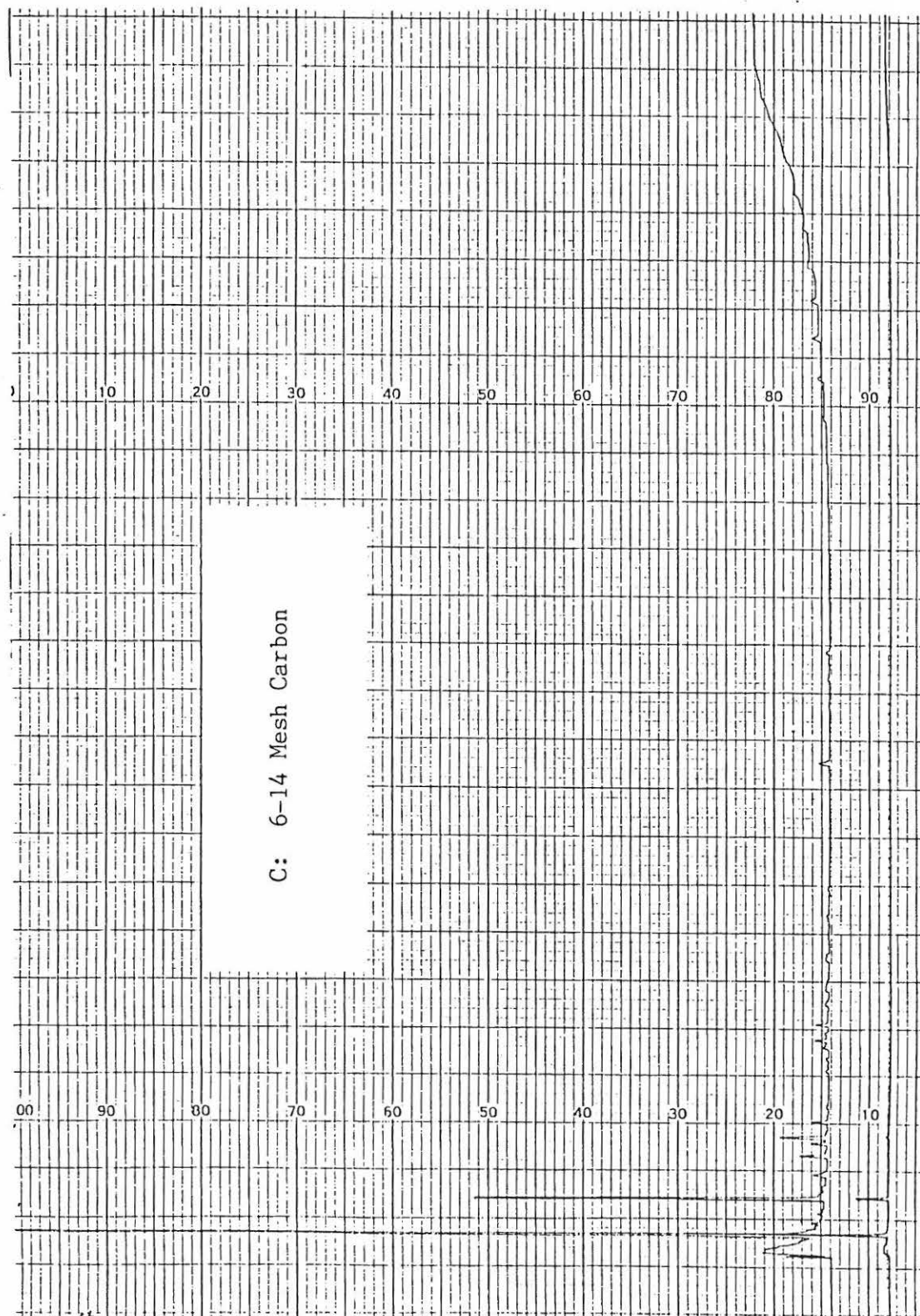
Activated charcoal is commonly used in the purge-trap technique for flammable liquid extraction from fire debris. Our laboratory procedure involves washing the charcoal tubes (each tube contains one inch of 50-200 activated charcoal) with one ml of carbon disulfide after the tubes are prepared. A number of quality control tests have shown that under our analytical procedure conditions, no measureable extractable residue remains after the washing. In the course of other experiments on charcoal, we had occasion to concentrate the wash solution and analyze it on a Varian Model 3700 gas chromatograph equipped with FID. A 0.75 mm x 60 m SPB-1 capillary column was used for the analyses with the following conditions: 60 degrees for 2 minutes, followed by a ramp of 10 degrees per minute to 250 degrees; helium flow rate of 36 ml/min. The chromatograms were recorded on a Linear Model 1200 dual pen recorder. The extraction conditions were as follows: three inches of Fisher Activated Carbon (50-200 mesh and 6-14 mesh) in 6 mm ID glass tube were washed with 1.5 ml of carbon disulfide; the resulting eluate was concentrated to 0.05 ml, and a two microliter aliquot injected.

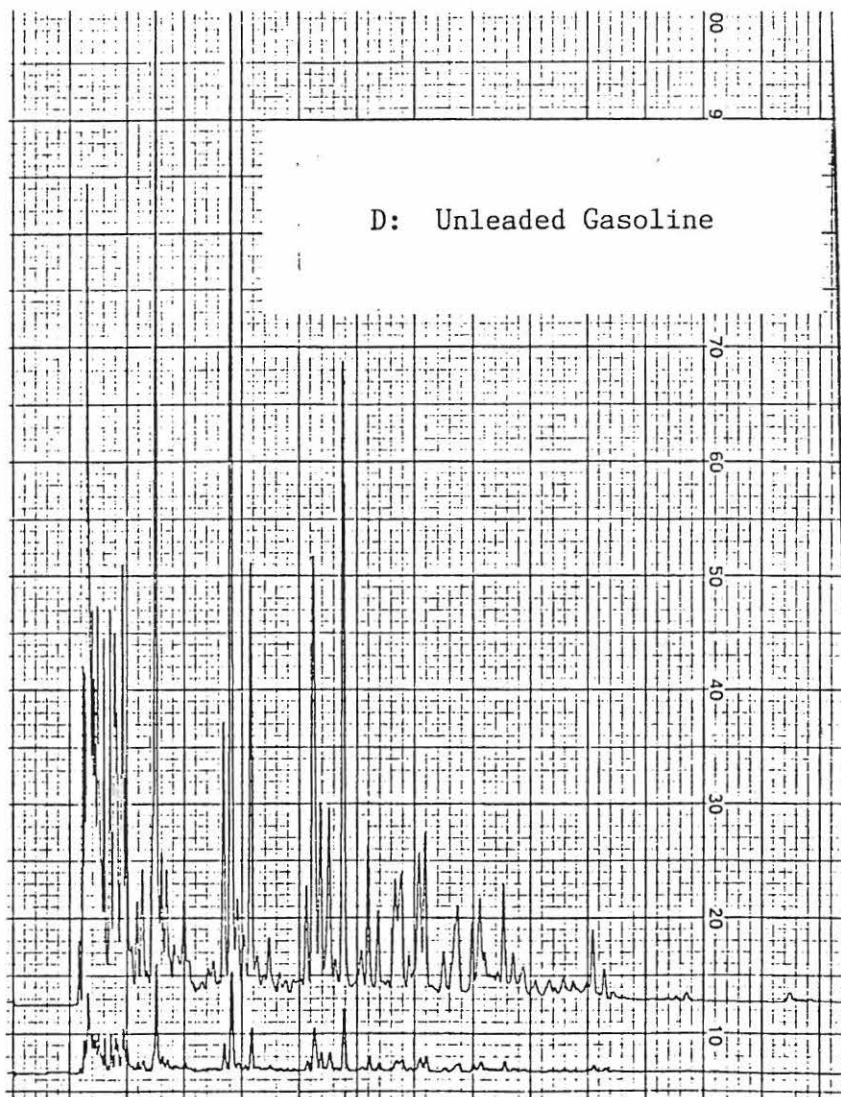
Chromatograms A and B show the results obtained with the concentrated eluate from two different cans of 50-200 mesh charcoal. The patterns for these two are quite similar, as are those for other batches of comparable charcoal. The results (C) for 6-14 mesh activated carbon are quite different, having considerably less background and a substantially different pattern. The chromatographs for gasoline and kerosene are included for comparison (D and E, respectively). The material in the 50-200 mesh charcoal resembles kerosene very closely and has additional components in the light-distillates range. Clearly, any procedure involving charcoal should be examined for possible interference from these residues.

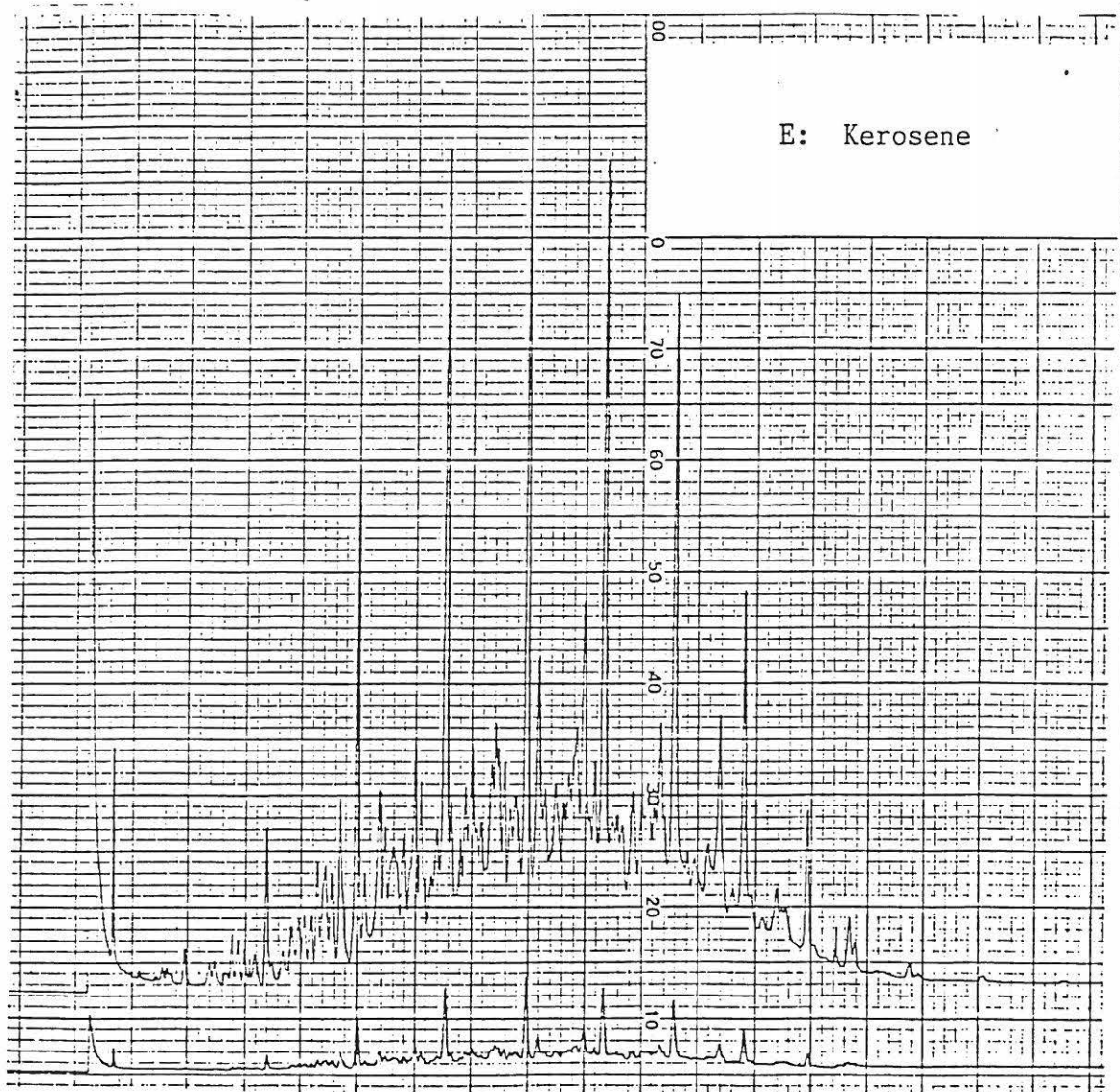
On a different note, the chromatograms for carbon disulfide in our laboratory always include a small peak following the major peak. Evaporation of the carbon disulfide causes this peak to increase in size. There appears to be no discussion in the literature of the identify of this peak, although it is invariably present in published chromatographs in which carbon disulfide is utilized as the solvent. If anyone has information concerning the identity of this component, please forward it to me.











A A Notes

*** ATF ANNOUNCES ARSON ACCELERANT DETECTION COURSES FOR 1987

The Bureau of Alcohol, Tobacco and Firearms will conduct two Accelerant Detection Classes in 1987 for state and local forensic examiners. The classes are scheduled for April 26 - May 1 and July 13 - 17, 1987. Enrollment is limited to 10 students per class.

The one-week course, conducted at ATF's National Laboratory Center (NLC) in Rockville, MD, emphasizes hands-on laboratory analysis utilizing all of the sample preparation techniques in common use today for arson examination. Lectures and discussions cover classifying accelerants, developing your own analysis scheme, accelerant comparison techniques, use of analytical techniques other than gas chromatography including GC/MS, pre-analysis clean-up techniques, refinery operations and proper evidence handling.

The course has been updated to place even more emphasis on the examiner's most challenging problem...interpretation of data. An additional practical exercise has been added. Recognition of incendiary devices and components has also been included in the lesson plans.

The course is designed for state and local chemists who perform, or will be performing, laboratory arson analysis. There is no tuition or registration fee, and all course materials are provided at no cost to the attendee. The ATF Laboratory will arrange a group rate (\$66 per night including tax) for all selected students at a hotel convenient to the NLC. All transportation, lodging, and per diem costs must be borne by the local department or individual. The U.S. Government per diem rate for the Washington, DC metropolitan area is \$112/day. Attendees should budget accordingly.

Those persons interested in applying for the school can obtain an application by contacting Rick Tontarski at ATF NLC, 1401 Research Blvd., Rockville, MD 20850 (202)294-0420. The application deadline is February 15, 1987. Applicants will be notified of their selection in March.

Please, keep those announcements and articles coming!!