BFG TECHNICAL DOCUMENT

BFG CHEMICAL CO.	ANALYTICAL		REPORT
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GC/MS ANALYSES ASSOCIATED WITH TEMPREL® HOSE FUMES

A problem at BFG Marion involving Temprel hose stock fuming which causes throat and eye irritation has existed since at least 1976 (see attachment). In 1976, the fumes generated during the manufacture of the Temprel hose were investigated by the Environ mental Health Department. While the fumes were not specifically characterized, certain observations were reported by the investigators. Diallyl phthalate (DAP), triallyl isocyanurate (TAIC) which has since been replaced by triallyl trimellitate (TATM) and peroxide related materials could be detected in air samples. However belief was expressed (see attachment) that no single Temprel ingredient, when heated, could produce the irritating fumes associated with Temprel stock. GC studies related the fumes to peroxide decomposition products and to allyl phthalate but these could not be confirmed in plant samples.

More recently, customers using Temprel hoses have complained about the irritating fumes resulting from the cutting of these materials with hot knives which can approach the pyrolytic decomposition temperature of these materials. These considerations and the fume problem at BFG Marion resulted in a planned study of the Temprel stock fumes and the fumes generated from the ingredients most likely to be responsible with TGA-DTA and GC/MS. S. W. Newell noted a definite lessening of the fumes when Uniflex 300 (a polyglycol ester derived from a mixture of 1,2-propane diol (major), 1,3-butane-diol, 1,4-butane diol and adipic acid(1)) was not used in the Temprel compound(2).

A series of compound formulations with dicumyl peroxide, lead silicate, [illegible], triallyl mellitate, Uniflex 300, diallyl phthalate, dicumyl [illegible] chlorinated polyethylene were prepared to cover the possible [illegible] of the ingredients used in Temprel hoses without [illegible] actual recipe. Of these, three compounded samples, [illegible] samples, and the plasticizers with and without dicumyl [illegible] were examined by GC/MS-headspace techniques. This report [illegible]izes the materials identified in these GC/MS-headspace studies.

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(1) The analysis of the Uniflex 300 material will be reported separately by J. L. Dorsch based on ^{13}C NMR measurements (see attachment).

(2) J. C. McCool communication to J. A. Nikora, 1/21/80.

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Experimental

The following compounds were heated in standard, evacuated headspace vials at 180°C for 20 minutes:

	3	7	10
CPE	100	100	100
BFM-1[a]	30	30	30
BFM-3[b]	12	12	12
TATM[c]	3.6	3.6	3.6
Uniflex 300[d]	10	--	--
DAP[e]	--	10	--
DOA[f]	--	--	10

[a] 60% lead silicate, 18% Desical and 22% CPE.
[b] 40% DiCup (40% dicumylperoxide on calcium carbonate) and 60% CPE.
[c] 74% triallyl mellitate on Microcel.
[d] Polyester based on a mixture of diols (primarily 1,2-propane diol) and adipic acid[1].
[e] Diallyl phthalate.
[f] Di-2-ethylhexyl adipate.

In addition to these compounds, the two masterbatches, BFM-1 and BFM-3, and the three plasticizers with and without dicumyl peroxide were examined under the same conditions. Pure dicumyl peroxide was obtained by extracting DiCup with diethyl ether and removing the ether by rotary evaporation. (Interestingly, too much BFM-3 masterbatch in a headspace vial ruptured the septum at 180°C and the escaping fumes generated from the dicumyl peroxide were irritating to the nose, throat, and eyes.)

At the end of the 20 minute-180°C heating period, the gas samples were [redacted] 5cc gas tight syringe and injected onto a 3.2mm x 4[redacted] packed with 80/100 mesh Porapak QS. The materials [redacted] gas chromatography were identified from their individual [redacted] spectrums by comparison with reference spectra.

Results and [redacted]

A series of GC/MS total ion current profiles (TICP's) were obtained from the headspace gases generated at 180°C. Figures 1 and 2 show the materials evolved from BFM-1 and BFM-3. The only volatiles expected from BFM-3, which contains dicumyl peroxide and chlorinated polyethylene, were expected to result from the peroxide decomposition. The following were identified:

Results and Discussions - (continued)

methane	methylethyl ketone
*ethane	benzene
water	toluene
methylchloride (CPE?)	C_2-benzenes
acetaldehyde	C_3-benzenes
iso-butene	α-methyl styrene
glycolaldehyde	C_4-benzenes
acetone	acetophenone

* At times, ethylene was also evident.

The aldehydes and acetophenone seemed to be the major irritants. This became evident when the pressure generated at 180°C ruptured the headspace vial's septum causing the gases to escape into the laboratory. Eye, nose, and throat irritation required the evacuation of the laboratory for about 15 minutes.

The volatile gases from BFM-1 (Figure 1) at 180°C can not be readily explained. None were expected since this masterbatch contains lead silicate, Desical and chlorinated polyethylene. BFM-1 was analyzed several times and even after steam stripping the column and obtaining a water-blank TICP, the same volatile materials were evident from this sample. These materials indicated that BFM-1 contained some dicumyl peroxide (possibly from preparing the material on the Brabender).

Figures 3-7 are the total ion current profiles obtained from the gases from the three different plasticizers with and without dicumyl peroxide at 180°C (except dioctyl adipate which was examined only as the mixture). Uniflex 300, a polyester, was shown by ^{13}C NMR to be based on a mixture of diols (primarily 1,2-propanediol with 1,3- and 2,3-butane diols) and adipic acid. The only major volatile material obtained from this was cyclopentanone. When mixed with dicumyl peroxide, the peroxide decomposition products were evident.

Examination of the diallylphthalate (Figure 5) volatile materials at 180°C showed the following volatile materials to be present: acetaldehyde, acrolein, allyl alcohol, and a material tentatively identified as diallyl ether. When the allylphthalate was mixed with the cumyl peroxide, no new products were observed. What was obtained (Figure 6) was the superimposition of the previously identified cumyl peroxide volatile components over those of the allylphthalate.

Results and Discussions - (continued)

Figure 7 shows the 180°C volatile materials obtained from a mixture of the plasticizer dioctyl adipate with cumyl peroxide. In addition to the cumyl peroxide decomposition products, only 2-ethylhexene and a small quantity of heptene and octene were identifiable. (The heating of these materials in vacuum and the nature of the analysis does not allow the clear distinction between 2-ethylhexene and 2-ethylhexanol, which could dehydrate under these conditions.)

Figures 8-10 present the GC/MS TICP's obtained from the headspace gases of compounds 3, 7, and 10. Surprisingly, the volatile gases obtained from the three plasticizer systems (with the exception of 2-ethylhexene) were no longer present at readily detectable levels. What was now found were the volatile materials related solely to the decomposition products of the dicumyl peroxide used in these systems. The following table presents a summary of the materials identified by these GC/MS-headspace techniques and the samples in which they were identified.

In looking at these results, the most obnoxious materials seem to be associated with the dicumyl peroxide decomposition products and the acrolein and allyl alcohol from the diallyl phthalate plasticizer. Since most of the irritating fumes are released during the lead stripping operation, it may be possible to alleviate most of the eye and throat irritation problems with the installation of more ventilation in the stripping and milling areas. Should these problems persist, the ALTC GC/MS laboratory has three small vacuum pumps (1L/min) for large scale area monitoring using charcoal and/or Tenax adsorbents to collect and concentrate organic vapors.

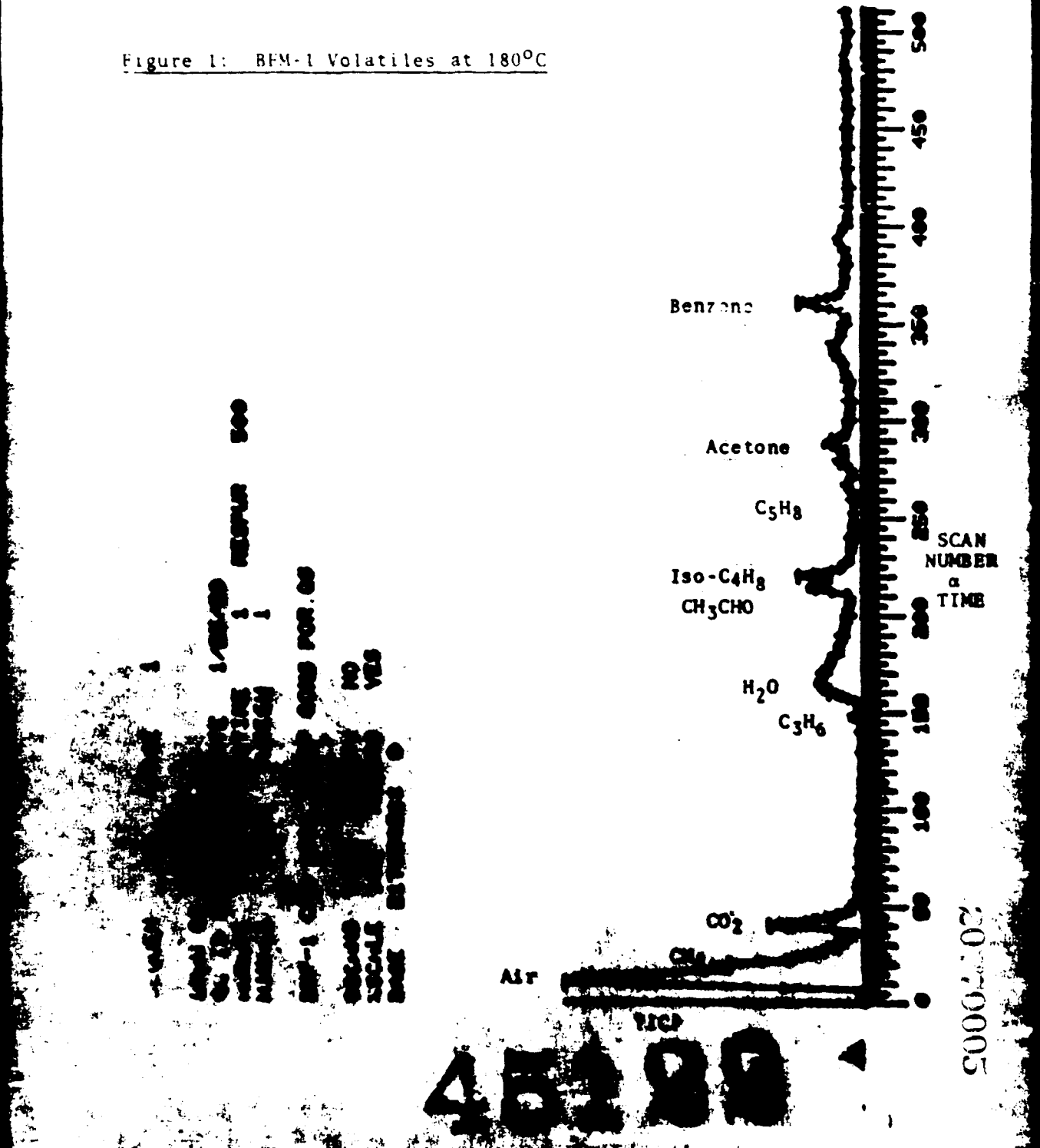
John A. Nikora

JAN/dmw

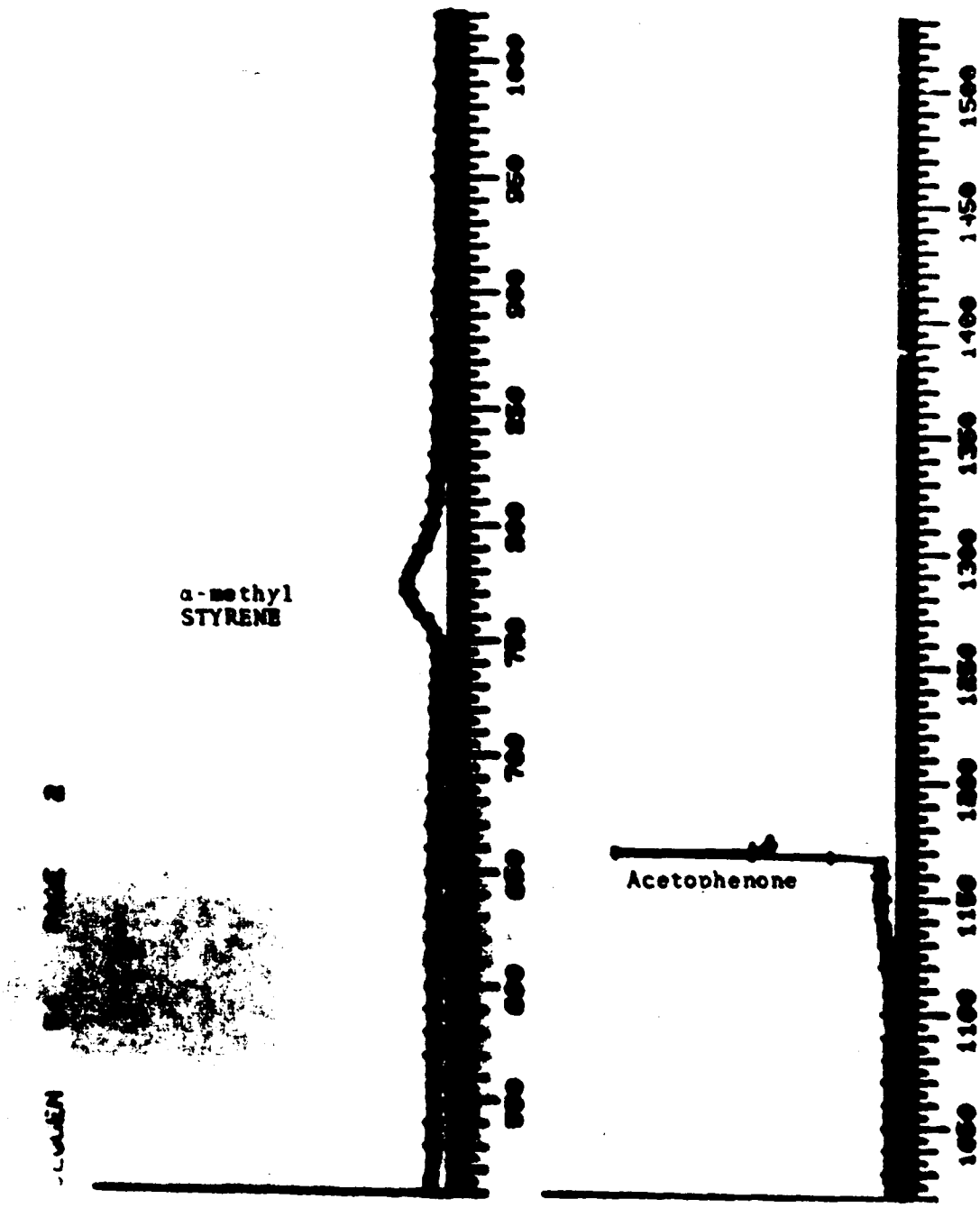
Attachments

cc: [redacted]
L. B. Crider
R. P. Koebel
J. L. Dorsch
J. B. Pausch - R. P. Lattimer (BRC)
J. C. McCool (Akron)
E. B. Katzenmeyer, Jr. - H. W. Dietz (Akron)
J. G. Quisenberry
C. H. Lufter - P. Zakriski (BRC)
S. W. Newell (Marion)
J. Messerly (BRC)
R. Varga (BRC)

Figure 1: BEM-1 Volatiles at 180°C

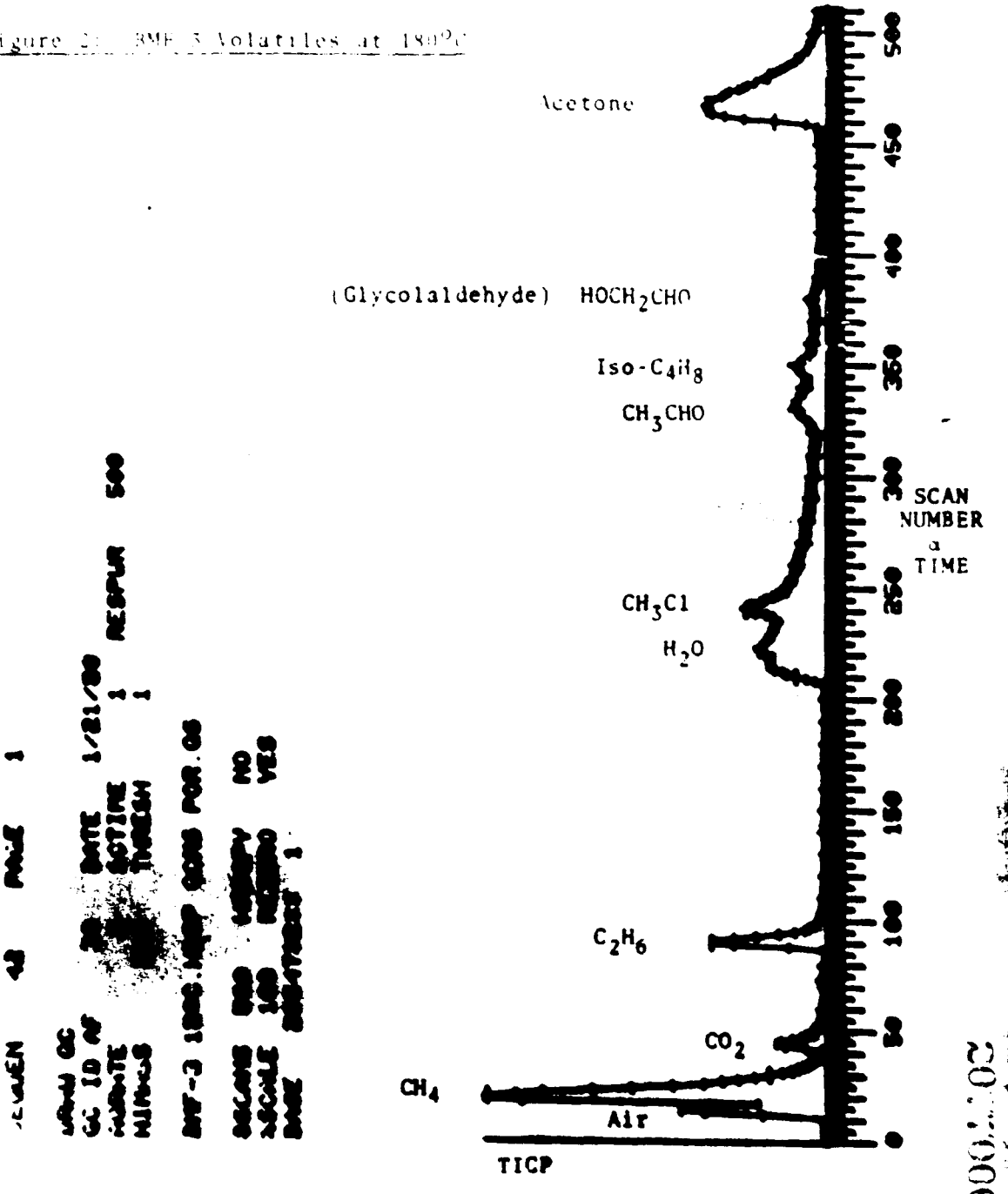


GC/MS Analyses Associated with Temprel® Hose Fumes



GC/MS Analyses Associated with Tempre1® Hose Fume

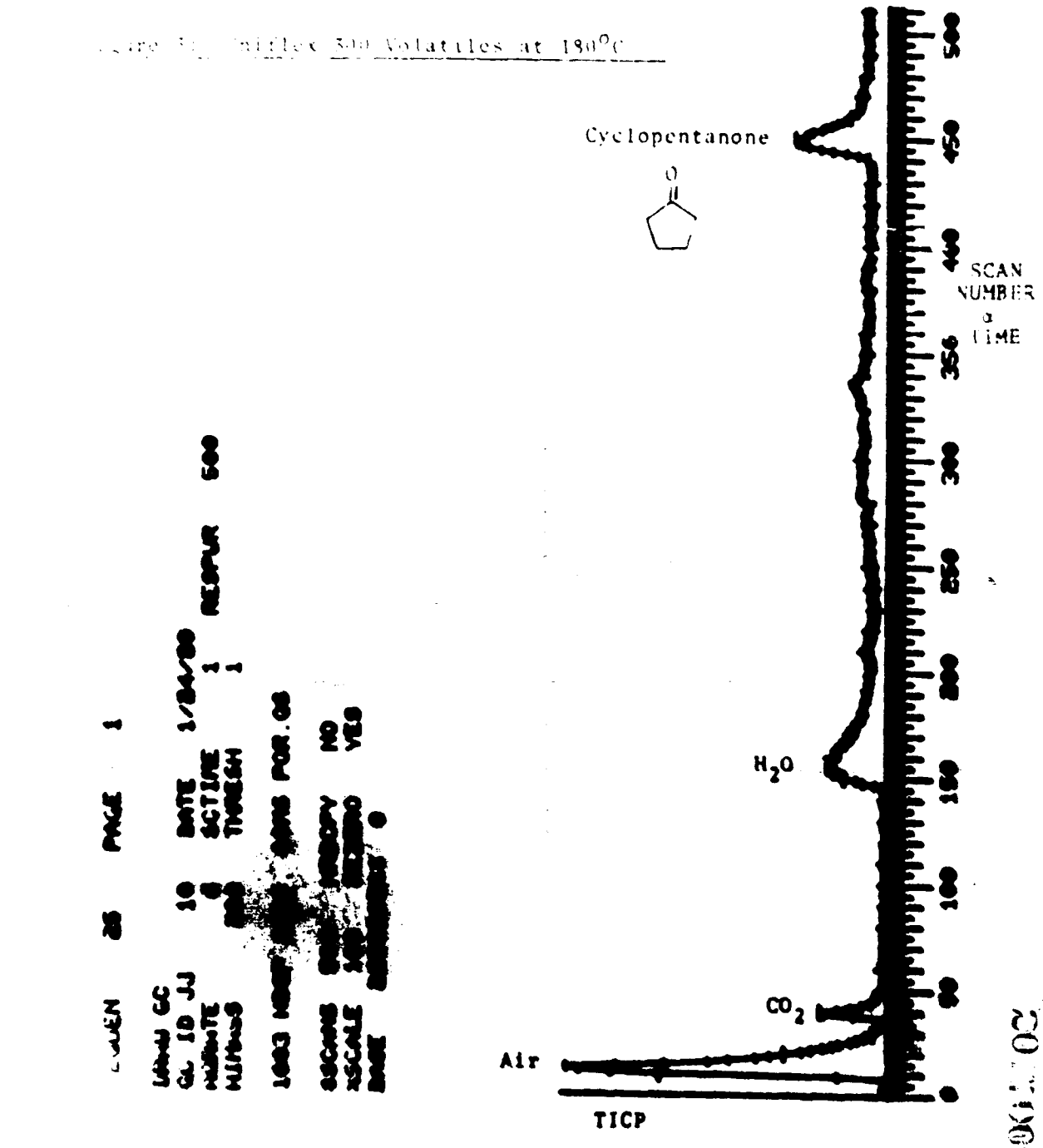
Figure 2: BMF-3 Volatiles at 180°C



GC/MS Analyses Associated with Temprel® Hose [illegible]

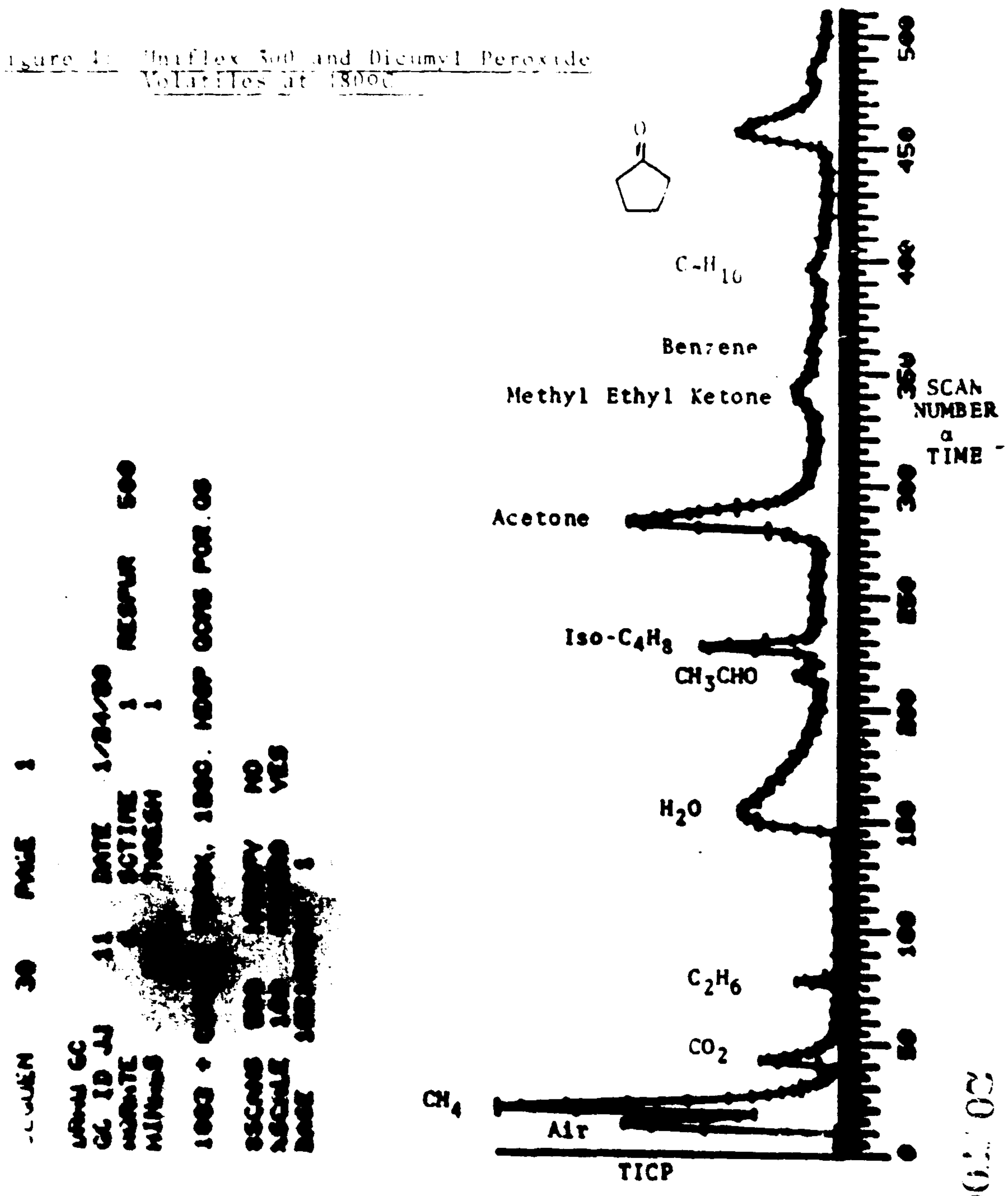
MS Analyses Associated with Temprel® Hose Fumes

Figure 5: Unaflex 500 Volatiles at 180°C



GC/MS Analyses Associated with Temprel® Hose Fumes

Figure 4: Uniflex 300 and Dicumyl Peroxide Volatiles at 180°C



GC/MS Analyses Associated with Temprel® Hose Fumes

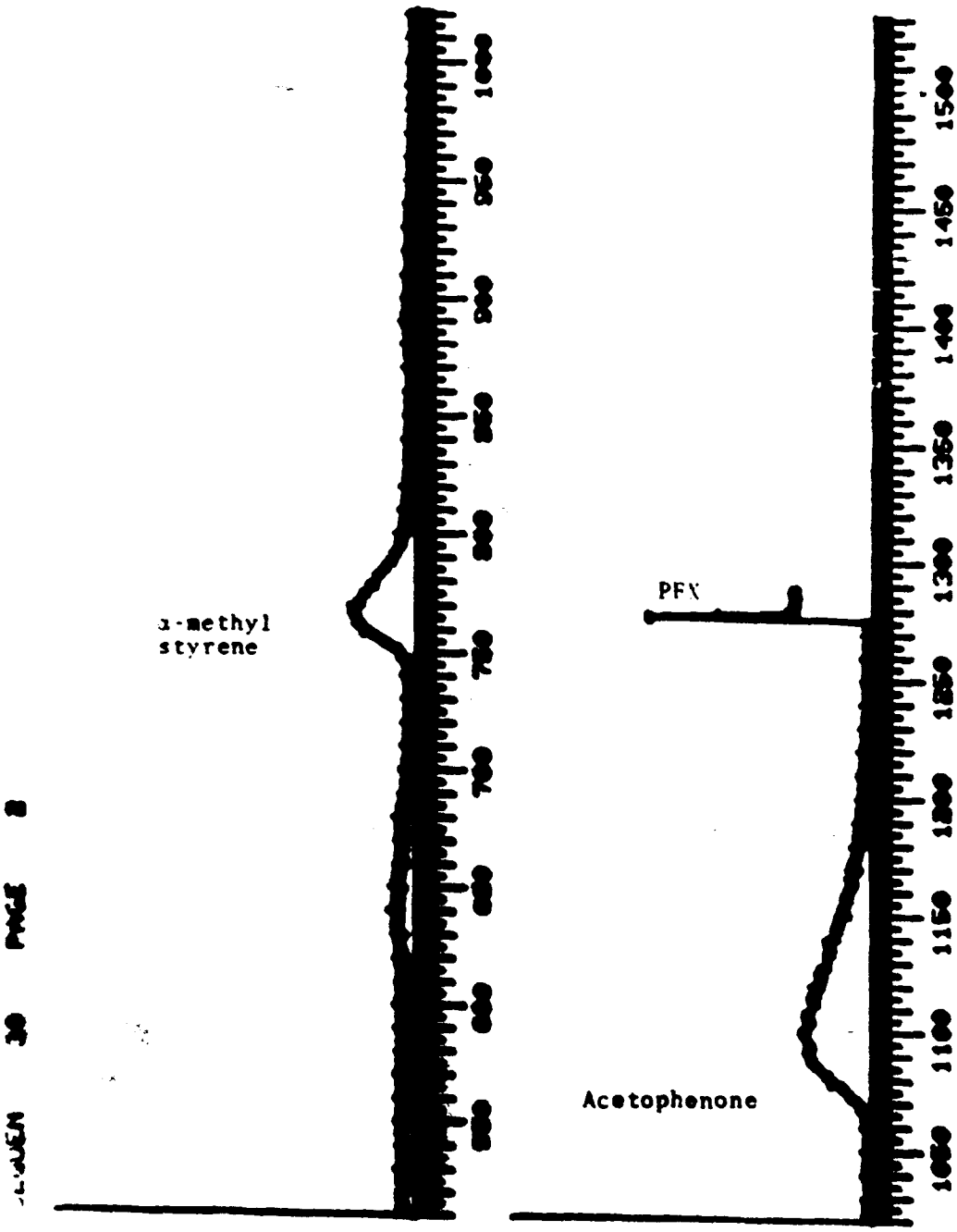


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Figure 3: DAP Volatiles at 180°C

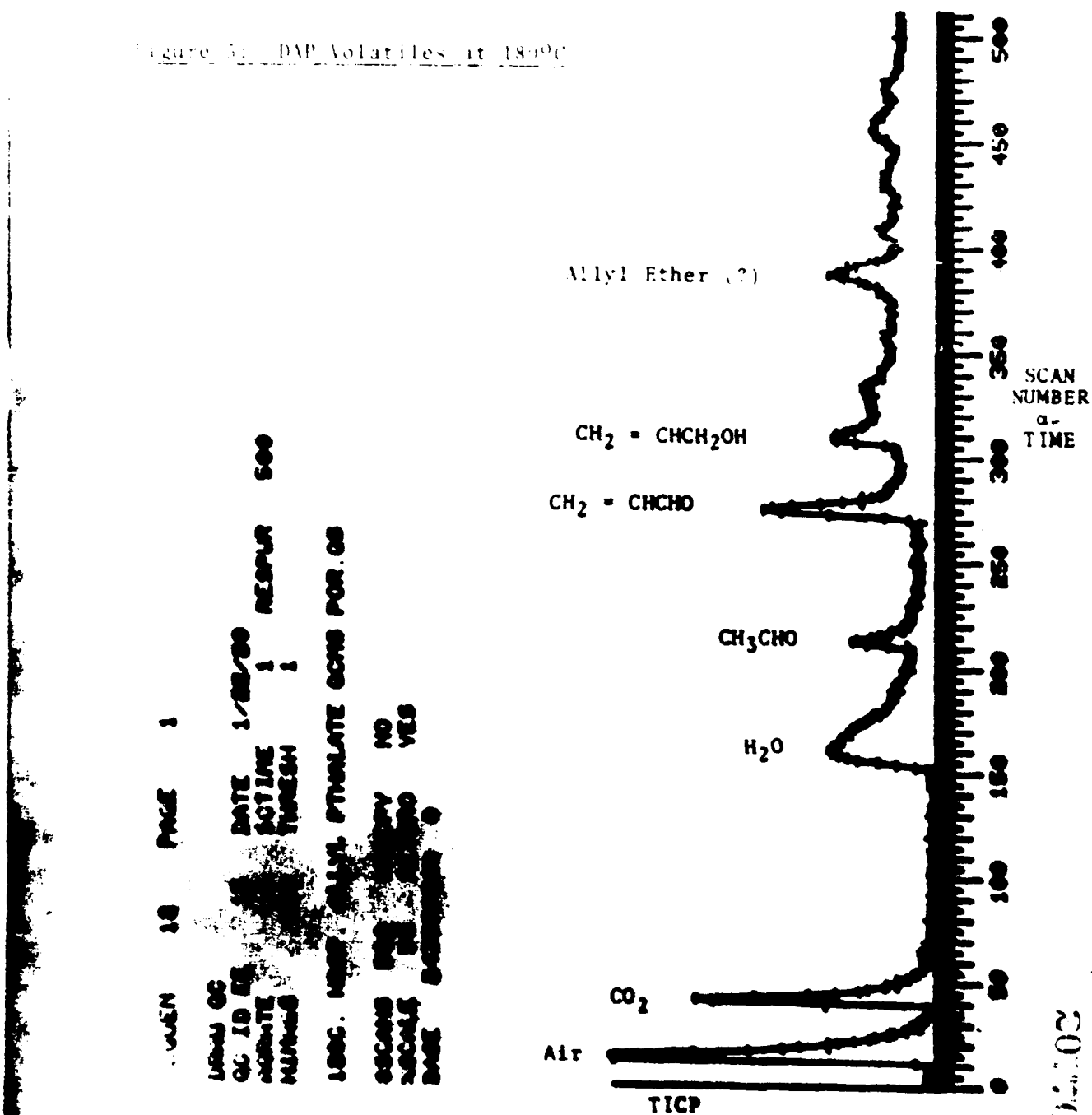
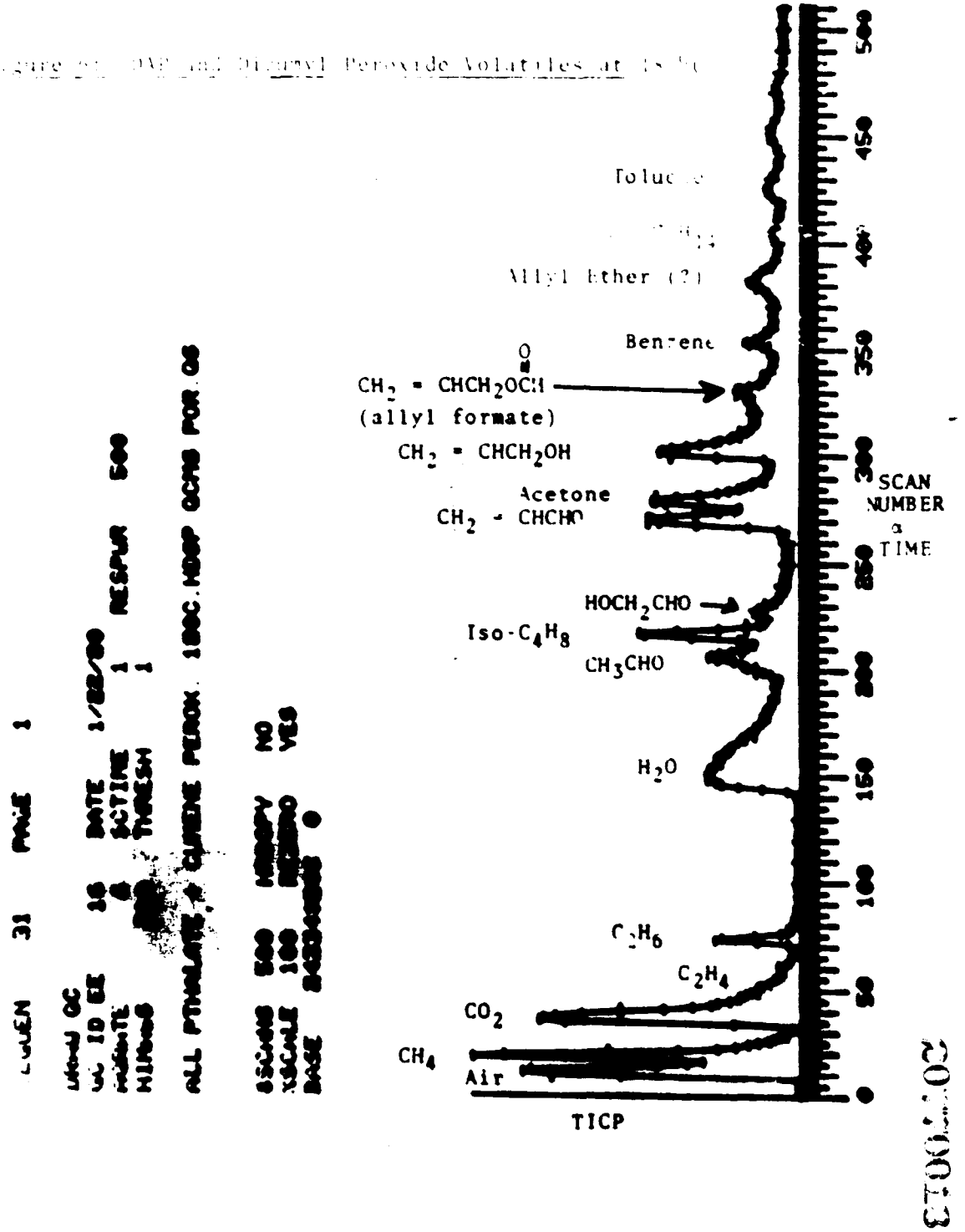


Figure 27. DVB and Diacetyl Peroxide Volatiles at 75 °C



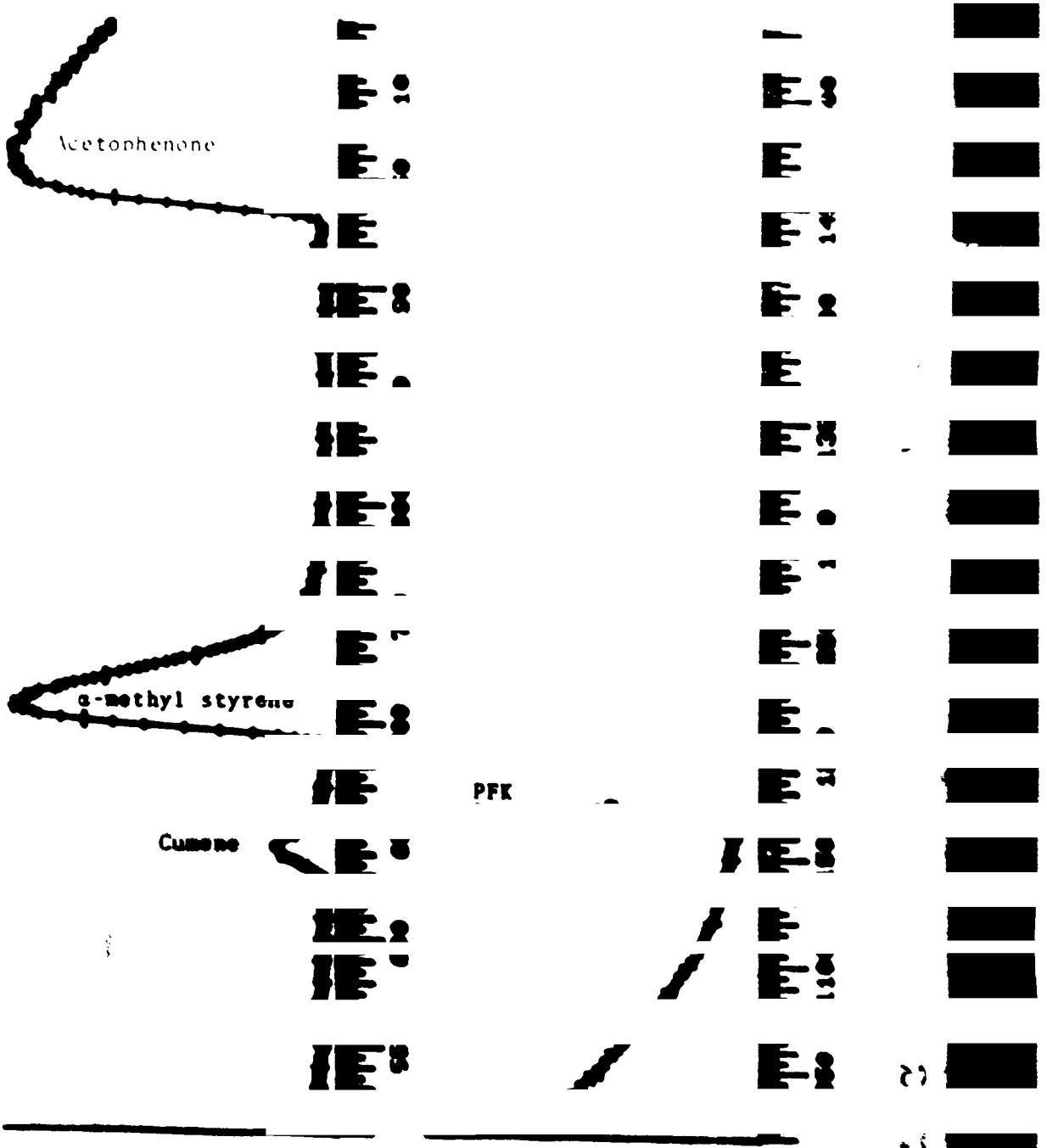

Acetophenone
α-methyl styrene
PFK
Cumene

Figure 7: Dioctyl Adipate and Dicumyl Peroxide Volatiles at 180°C