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RECOVERY OF VOLATILE ORGANICS FROM SORBENT TUBE SAMPLING SYSTEM--ETC(U)
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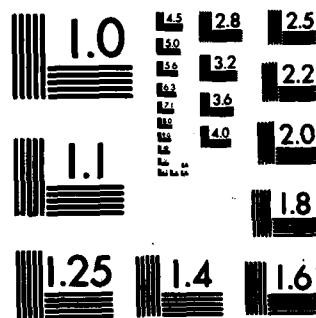
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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER SAM-TR-80-22	2. GOVT ACCESSION NO. AD-A090 954	3. RECIPIENT'S CATALOG NUMBER
4. AUTHOR (and Subtitle) RECOVERY OF VOLATILE ORGANICS FROM SORBENT TUBE SAMPLING SYSTEMS	5. TYPE OF REPORT & PERIOD COVERED Progress Report Jan 1978 - Nov 1979	6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR William W. Lackey, Charles L. Martin, James P. Conkle, and Richard L. Miller	8. CONTRACT OR GRANT NUMBER(s)	
9. PERFORMING ORGANIZATION NAME AND ADDRESS USAF School of Aerospace Medicine (VNL) Aerospace Medical Division (AFSC) Brooks Air Force Base, Texas 78235	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 62202E 793011137	
11. CONTROLLING OFFICE NAME AND ADDRESS USAF School of Aerospace Medicine (VNL) Aerospace Medical Division (AFSC) Brooks Air Force Base, Texas 78235	12. REPORT DATE August 1980	
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)	13. NUMBER OF PAGES 11	
	15. SECURITY CLASS. (of this report) UNCLASSIFIED	
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Dimethylnitrosamine Gas chromatograph/mass spectrometer/data system Sorbent tube sampling		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Comparative data are presented on the recovery of organic compounds (vapors) from solid sorbent (Tenax-GC) sampling tubes by thermal desorption of the tube contents (a) directly onto a packed gas chromatographic column, vs. (b) onto an unpacked precolumn loop for subsequent injection into the gas chromatograph. Twenty to eighty percent increases in flame ionization detector (FID) response were obtained for a limited selection of compounds which were desorbed directly on-column. The apparent overall increase in system sensitivity allowed detection and identification of compounds at lower levels than were previously		

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20. ABSTRACT (Continued)

possible. A table of compound recoveries lists the recoveries from the Tenax-GC sorbent for the standards used in this experiment.



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RECOVERY OF VOLATILE ORGANICS FROM
SORBENT TUBE SAMPLING SYSTEMS

INTRODUCTION

Recently this laboratory reported the development of a sorption tube sampling system for trapping trace-level volatiles for analysis by gas chromatograph/mass spectrometer/data system (GC/MS/DS) (2, 9). Further, these previous reports described the methods and procedures used in the GC/MS/DS analysis of samples, in which the sorbent sample tube was temperature-desorbed into a precolumn loop that was precooled by liquid nitrogen (LN₂). This paper describes modifications made to the sample desorption procedure which allows direct on-column desorption of the volatile organics. Data presented on sorbent sample recovery efficiency on-column versus precolumn loop demonstrate an improvement in methodology.

MATERIALS

The GC/MS/DS instrumentation (Fig. 1) is a DuPont mass spectrometer (21-491, Lot 5), data acquisition system (21-094), and gas chromatograph (Varian 1400) modified to permit gas-sample injection by way of a precolumn loop. This sample loop introduction system, in use in this laboratory since Feb 1967 (10), has more recently been reported by Bertsch et al. (1) and Pellizzari et al. (12) as an approach to analysis of environmental samples by GC/MS/DS. Figure 2 shows the precolumn loop (covered by a heat blanket), a system of valves including the two 4-way loop valves, a pressure transducer, a flowmeter, and a Tenax sorbent sample tube with the clamshell heater block in place for sample desorption. The use of this sample introduction system, along with the calculations involved, has been discussed elsewhere (9).

The modification made to the GC to permit on-column desorption consisted of installation of a 3-way valve in the column carrier gas line to allow switching the carrier gas from the sample loop, described above, to a Cajon VCR male fitting installed near the GC injection port on the front of the instrument (see Fig. 3). The arrangement was devised so that when sorbent sample tubes were being run, the GC could be converted from its normal configuration to one in which the sorbent tube was attached to the injector port by an adapter machined from hex aluminum stock with a Cajon VCR male fitting on one side and proper threads on the other end to replace the septum nut.

METHODS

Sorbent tubes were prepared for GC/MS/DS analysis by loading the tubes with known amounts of various organic compounds prepared from gas standards obtained from Matheson Gas Products. The concentration of each compound used is shown in the first column of Table 1. Shown across the top of the table is the volume of standard gas processed through the sorbent tubes, as measured by a Wet Test



Figure 1. View of the analytical system: gas chromatograph (Varian 1400)/mass spectrometer (DuPont 21-491)/data acquisition (DuPont 21-094).

Meter (Precision Scientific Co.). In the case of n-nitrosodimethylamine (NDMA), standards of various concentrations (0.01 to 5.0 $\mu\text{g}/\mu\text{l}$) were made up in triple distilled water from which sorbent tubes were doped with various volumes. Further, the NDMA doped tubes were flushed at room temperature with helium (He) at 1 liter/min for 20 minutes to remove most of the water prior to thermal desorption into the GC precolumn loop or directly on-column at the injector port.

The GC column used was a microbore tube (0.7 mm ID x 3.2 mm OD x 3m) packed with Porapak Q (120-150 mesh). The column effluent was split 1 part to the GC flame ionization detector (FID) and 8 parts to the MS source via a stainless-steel jet separator. The 8 to 1 split was used to partly overcome the problem of rather poor MS sensitivity to NDMA. Quantitation of the samples was accomplished by use of a HP 3352B Laboratory Data System which estimated peak areas from the FID response.

The method of analyzing sorbent tubes via the precolumn loop has been described elsewhere (9); thus, this report will detail only the analysis of sorbent tubes directly on-column by way of the injector port. After cooling the GC oven to room temperature, the GC/MS isolation valve was closed to prevent admitting air to the MS source by way of the GC column in the next steps. The GC oven was cooled with LN_2 to approximately -100°C ; the septum nut and septum were then removed and replaced with the sorbent tube adapter, sorbent tube, and connecting carrier gas line as shown in Figure 3. As soon as the connecting fittings were tightened, the 3-way valve in the carrier gas line was switched so that helium flowed through the sorbent tube to the GC column while the clamshell heating block was attached to desorb the tube contents. The sample tube was heated to 280°C in 10 min and then maintained at 280°C for another 10 min. At the end of the 20-min desorption period, the heating block was removed and the 3-way valve switched back to its original position so that the carrier gas

TABLE 1. PERCENT RECOVERY FROM SORBENT (TENAX-GC) TUBE

Compound	$\mu\text{g/liter}$	Liters of Gas STD ^a Used					
		0.25	0.50	0.75	1.00	1.50	2.00
Ethene	0.285	18.2	5.3	8.3	3.9	3.1	3.1
Ethane	3.572	13.2	6.1	4.5	3.2	2.2	1.8
Chloromethane	5.103	73.3	54.5	43.4	31.1	21.7	19.0
Acetone	2.640	71.8	71.3	75.7	76.2	74.4	78.0
Chloroethylene	10.632	66.4	66.8	62.9	55.1	40.4	38.2
Chloroethane	11.341	85.6	92.8	88.7	90.5	79.1	83.9
Ethyl ether	8.865	64.6	70.7	67.3	69.5	67.8	68.0
Benzene	3.570	76.4	64.3	68.3	71.0	66.4	70.1
N-Hexane	3.930	70.1	63.8	68.6	70.3	66.8	70.5
Toluene	4.200	70.5	62.2	65.8	68.0	63.9	67.1
1,2-Dichloroethane	7.814	66.9	72.2	69.9	70.6	70.2	70.1
Means ^b		72.3	71.0	72.0	73.7	69.8	72.5

^aGas standards were prepared in concentrations shown in the first column from standards obtained from Matheson Gas Products (#B-4404 and cyl #J-56040, 3-11-76).

^bMeans calculated without ethene, ethane, chloromethane, and chloroethylene (see body of report).

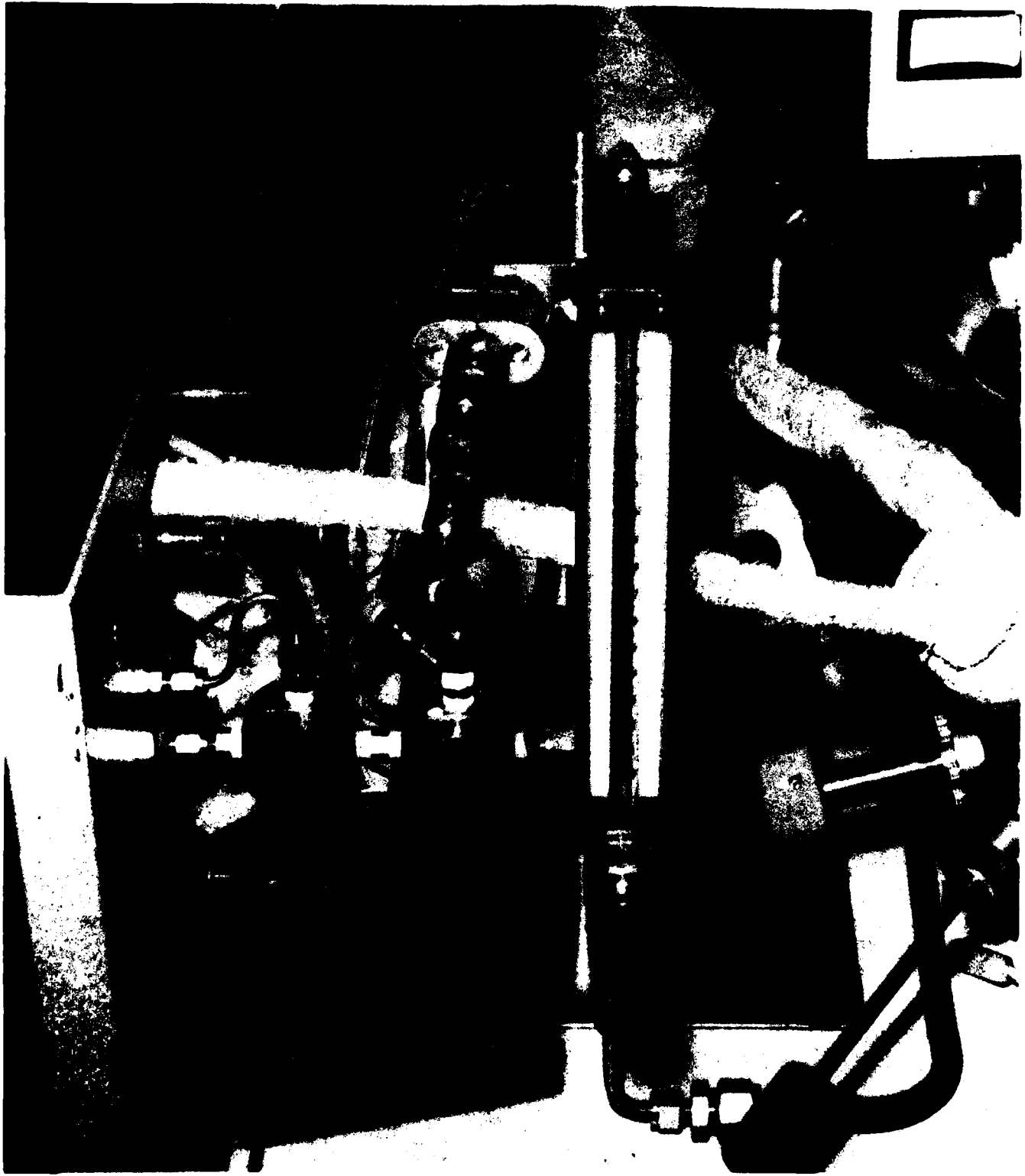


Figure 2. Gas sample loop introduction system of GC/MS/DS depicting sample injection after sorbent tube desorption into the loop.



Figure 3. Sorbent tube (Tenax-GC) connected for direct on-column (precolumn) desorption.

flowed through the injector block in the normal manner. The next step was to raise the GC oven temperature from -100°C to 240°C at approximately $10^{\circ}\text{C}/\text{min}$. The oven temperature rise during the early part of the run was controlled by the ambient air admitted to the oven, and at 0°C the GC linear programmer controlled the temperature at $10^{\circ}\text{C}/\text{min}$ to 240°C . Starting the GC at -100°C allowed the low molecular weight gases (Ne, N_2 , O_2 , Ar, CO, CH_4 , CO_2 , and N_2O), usually of little interest in the MS analysis, to clear the column prior to the elution of the hydrocarbons. This procedure enhanced the library search identification of the various GC peaks because the mass spectra were not masked by mass contributions of the low molecular weight gas. If there were an interest in the presence or absence of light gases, the GC/MS isolation valve was opened before the oven temperature was allowed to rise from -100°C ; otherwise, the GC/MS valve was not opened prior to 0°C . The presence of light gases may be monitored by observing the display register of the data system computer during the GC run. Even though there is little or no GC flame ionization response to these light gases, they do have an MS response and may be recorded by the MS data system if desired.

The FID responses or GC calibration for the various compounds, except for NDMA, was accomplished by using a standard tube designed to replace the sorbent tube in the clamshell heating block. The standard tube was stainless steel, 63.5 mm OD x 13.97 cm long, equipped with ball valves on each end which resulted in a 2.7-ml volume, including the internal volume of one ball valve. The tube was charged with a calibration gas standard by attaching it to a system

which allowed evacuation of the tube to 10^{-4} torr, then pressurizing with a calibration gas to a known pressure of one or more atmospheres. After charging the standard tube, it was attached to the injector port to be run similar to a sorbent tube. The main difference was the 150°C temperature limit to which the tube assembly could be heated due to the ball valve seals. This temperature was more than sufficient for the compounds of interest as standards.

The comparative recovery rates for each method of analysis are shown in Figures 4 and 5 for eight representative organic compounds. The data points shown in Figures 4 and 5 are micrograms of compounds added to the sorbent tube versus the FID response in area units from the HP 3352B integrator. The curves drawn through the data points to estimate an average response were derived by the least-squares method. Further, the smooth curves of Figure 6 were calculated from the least-squares curves shown in the previous figures so that Figure 6 is a summary of the comparative data; i.e., sample introduction via direct on-column versus precolumn loop. Additional information, such as recovery of standards from Tenax-GC sorbent, was available from the data shown in Figures 4 and 5 if FID response of the standards was considered. Using the FID responses for the various standards which were obtained from the standard tube calibration runs, estimates of recovery are made from the direct on-column data and the percent recoveries in Table 1 are calculated from the known amounts doped on each tube.

DISCUSSION

The development of the improved methodology described in this report was prompted by the lack of GC/MS sensitivity to NDMA and by the self-imposed requirement by the U.S. Air Force that the presence of NDMA in air samples from field installations would be confirmed by GC/MS for positive identification. This requirement was established by Air Force Deputy Assistant Secretary for Environmental Affairs in November 1975 and is in agreement with current philosophy that GC/MS confirmation of NDMA is highly desirable (5-7, 11, 12). Further, other investigators may advocate instrumentation such as the Thermal Energy Analyzer (TEA) for NDMA analysis; however, they use GC/MS for confirmation in their own research (3, 4), all of which indicates the importance of maximizing GC/MS sensitivity when analyzing for NDMA. Figures 4, 5, and 6 show there is an advantage to desorption of tube samples directly on-column, regardless of the compounds expected in the analysis. Evidence indicates that with the improved sample introduction to the GC/MS system, field sampling times with sorbent tubes may be reduced by as much as 30%-40% without altering the results of the analysis. Desorption directly on-column does not make the resulting analysis any more accurate than the results obtained by using the sample loop introduction method. Each method requires that calibration standards be run in the same manner as the experimental or field samples containing unknowns.

A bonus from this experiment is the recovery data shown in Table 1 which supplements the works of Bertsch et al. (1) and Pellizzari et al. (11). Bertsch, using an LN_2 cooled precolumn loop into which he desorbed Tenax-GC tube samples of freeway air pollution, reported trapping all substances at better than 90% except for benzaldehyde and acetophenone; and, that there was a partial loss of substances eluting before benzene due to "breakthrough" of the sorbent bed. Pellizzari reported 80%, 90%, and 95% collection efficiencies for three different synthetic air-vapor mixtures for Tenax-GC cartridge sample evaluation. Table 1 shows approximately 72% recovery when ethene, ethane, chloromethane, and chloroethylene are deleted from the averaging. These four

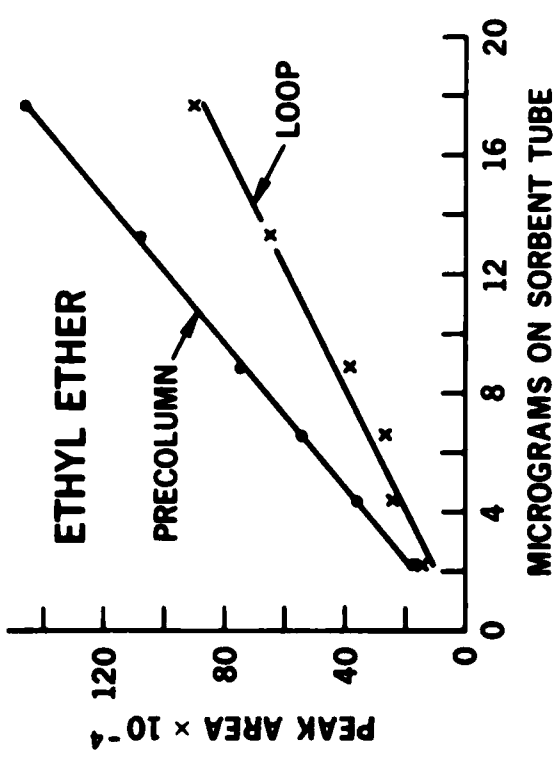
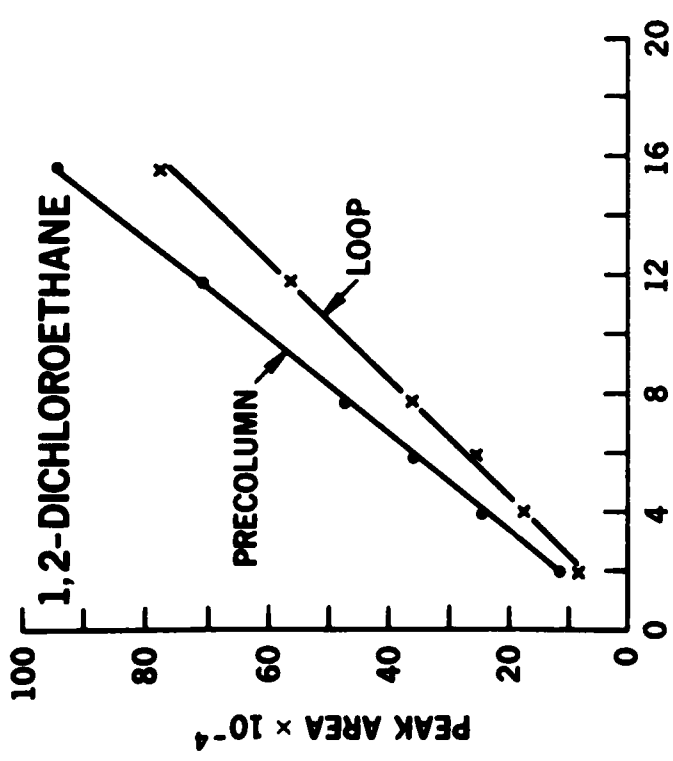
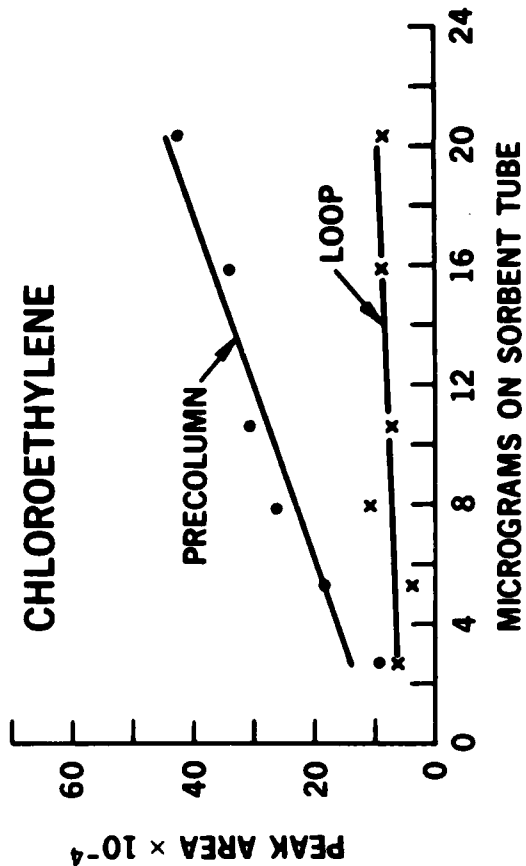
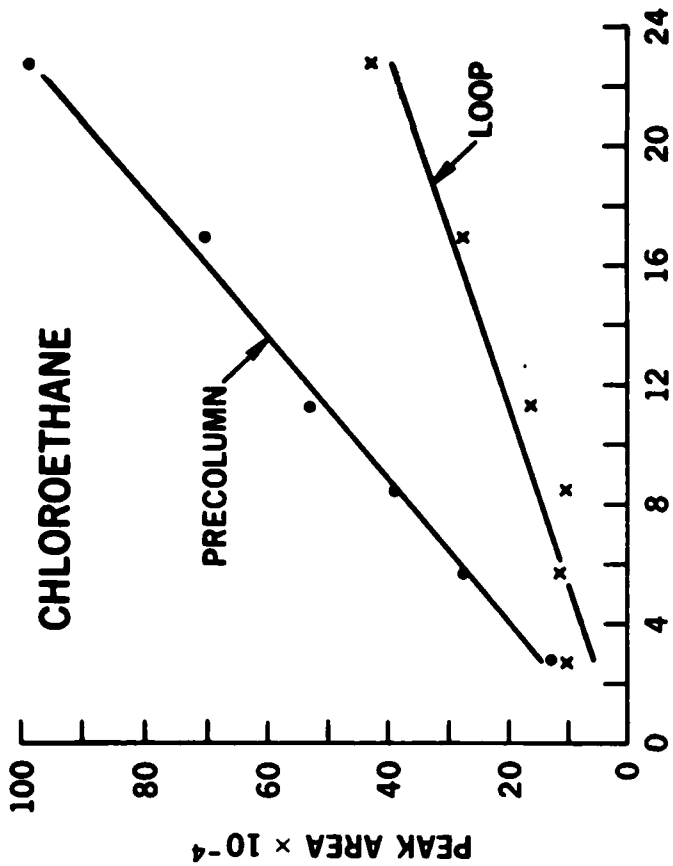


Figure 4. Data from doped sorbent (Tenax-GC) sample tubes desorbed and analyzed via GC sample loop and direct on-column (precolumn). Peak areas $\times 10^{-4}$ are area units from an HP3352B data system (FID response).

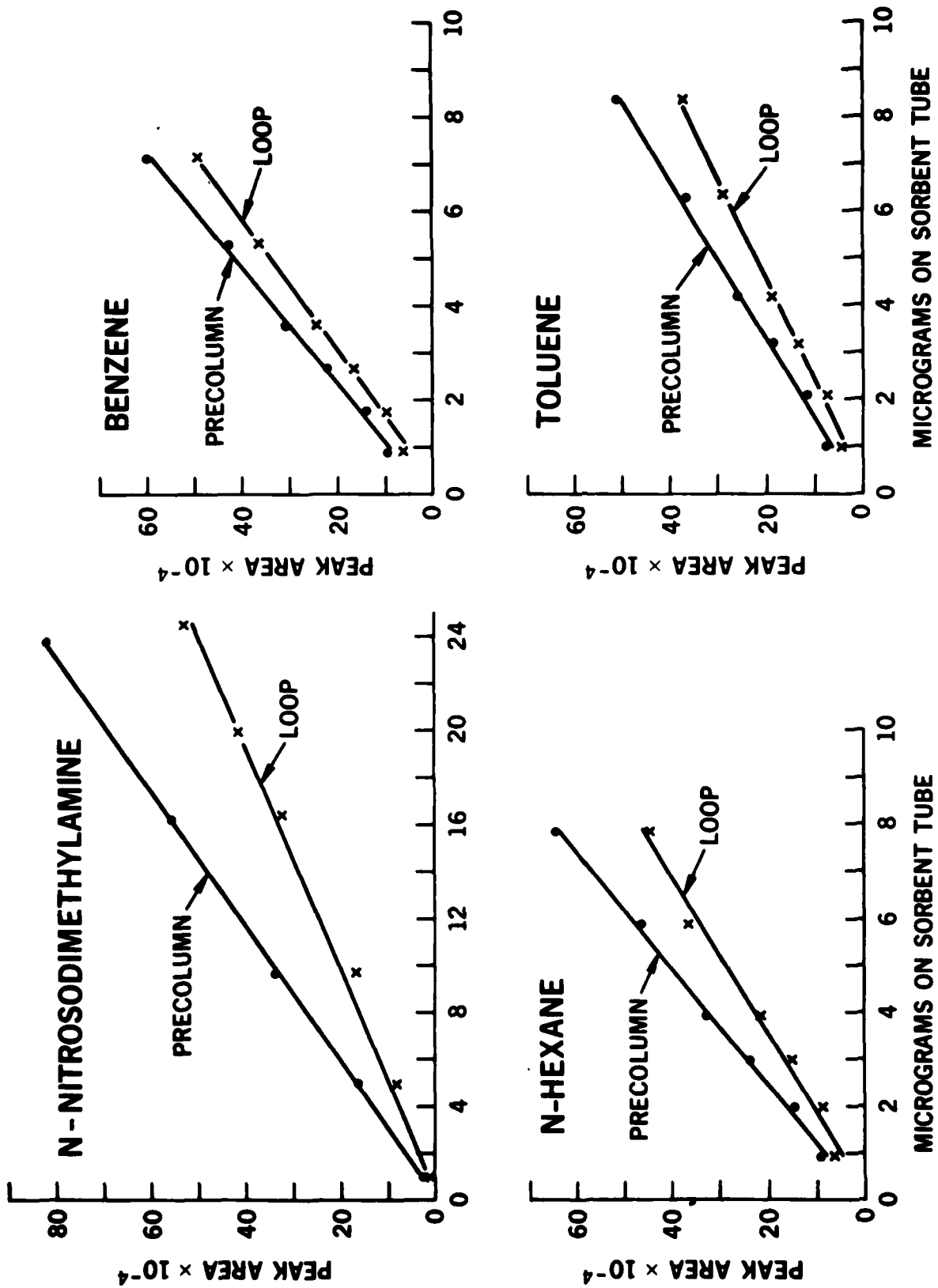
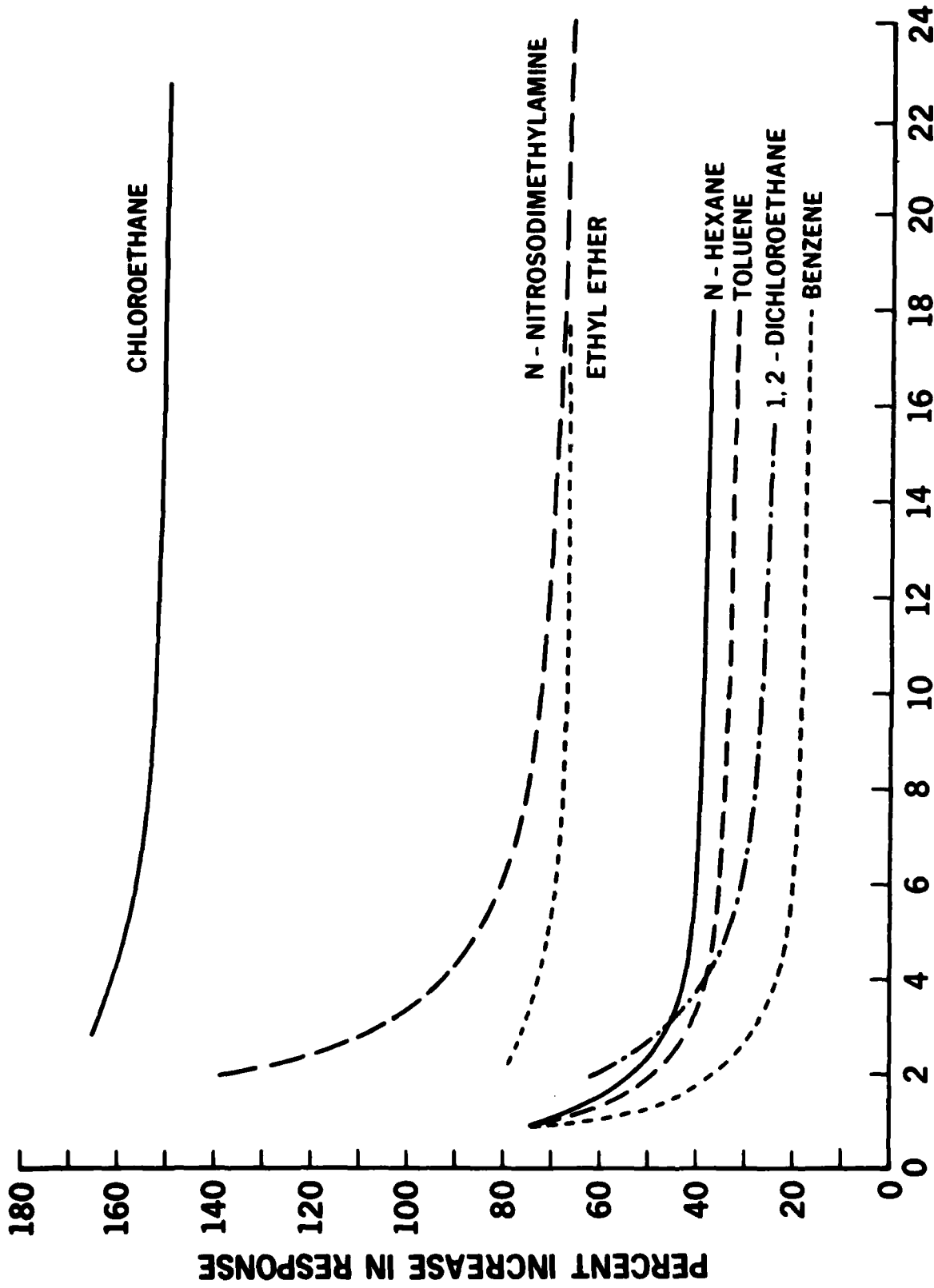


Figure 5. Data from doped sorbent (Tenax-6C) sample tubes desorbed and analyzed via GC sample loop and direct on-column (precolumn). Peak areas $\times 10^{-4}$ are area units from an HP3352B data system (FID response).



MICROGRAMS ON SORBENT TUBE

Figure 6. Percent increase in response of direct on-column (precolumn) versus sample loop calculated from data curves in Figures 4 and 5.

compounds show very definite trends of reduced recovery as increased volumes of standard gas flowed through the tubes in the process of doping the tubes. All of this suggests that 10% to 20% of the compounds in Table 1 may not have been desorbed from our sample tubes, or that the trapping efficiency is less than that suggested by the literature cited, or a combination of both. NDMA is of special interest (3-7, 11, 13) and is discussed in detail elsewhere (8).

CONCLUSIONS

Direct on-column desorption of our Tenax-GC sorbent tubes is an improved methodology not only from the standpoint of reducing losses during sample introduction to the GC, but it saves analysis time and eliminates the problems connected with sample introduction via the loop; i.e., interruption of sample transfer due to ice plugs in the loop from sample water vapor (1, 9, 12) and the risk of liquid oxygen formation in the loop if a leak to the ambient air should exist during sample transfer (9). The importance of the reduction in loss of sample during sample transfer is that it, in effect, results in an overall increase of sensitivity of the GC/MS system which allows detection and identification of hazardous compounds such as NDMA at lower trace levels.

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