Method no.:	66
Matrix:	Air
Target concentration:	10 ppm (30 mg/m^3) (OSHA PEL)
Procedure:	Air samples are collected by drawing known volumes of air through sampling tubes containing coconut shell charcoal. Samples are desorbed with acetone and analyzed by gas chromatography using a nitrogen/phosphorus detector.
Recommended air volume and sampling rate:	10 L at 0.2 L/min
Reliable quantitation limit:	0.02 ppm (0.045 mg/m^3)
Standard error of estimate at the target concentration: (Section 4.5)	7.4%
Status of method:	Evaluated method. This method has been subjected to the established evaluation procedures of the Organic Methods Evaluation Branch.

Date: August 1987

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1. General Discussion

1.1 Background

1.1.1 History

This procedure was evaluated in order to overcome shortcomings in the dimethylformamide (DMF) sampling and analytical method previously used by OSHA. The previous method required the collection of samples on silica gel, desorption with methanol, and analysis by gas chromatography (GC) using a flame ionization detector (FID). (Ref. 5.1) The desorption efficiency of DMF from silica gel was low and not constant for low sampler loadings. A 50-L air sample was required in order to obtain a sampler loading at the PEL which would provide a desorption efficiency of at least 75%.

A procedure which required the collection of samples with charcoal, desorption with acetone and analysis by GC using a nitrogen/phosphorus detector (NPD) (Refs. 5.2 and 5.3) was evaluated. Since the desorption efficiency of DMF from charcoal with acetone was 91% over the range of 0.02 to 2 times the PEL, valid analyses of lower sampler loadings are more easily attainable with this procedure.

1.1.2 Toxic effects (This section is for information only and should not be taken as the basis of OSHA policy.)

DMF is a moderately toxic compound which can cause liver damage. Occupational exposure normally results from inhalation or skin absorption. Symptoms of short-term exposure to DMF are abdominal distress, colicky abdominal pain, loss of appetite, nausea, vomiting, constipation, diarrhea, facial flushing (particularly after alcohol ingestion), agitation and increased blood pressure. Skin contact may cause irritation with the possibility of a rash upon prolonged or repeated contact (Ref. 5.4). Eye contact produces temporary conjunctivitis and transient corneal damage in animals (Ref. 5.5). The oral LD_{50} for rats is 3500 mg/kg, and the estimated lethal dose for humans is 10 g (Ref. 5.6).

Thirteen workers exposed to concentrations below 20 ppm and occasionally to higher levels for up to 32 weeks complained of nausea, vomiting, and colic; some cases of hepatomegaly were detected. A worker who was splashed with the liquid over 20% of his body surface initially suffered only dermal irritation and hyperemia; abdominal pain began 62 hours after the exposure and became progressively more severe with vomiting; the blood pressure was elevated to 190/100; the effects gradually subsided and were entirely abated by the seventh day after the exposure. (Ref. 5.4)

1.1.3 Workplace exposure

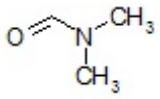
In 1979, world production of DMF was 225,000 metric tons with nearly half of the total being produced in Europe. Approximately 48,000 tons were produced in the United States (Ref. 5.5.). No estimate vas found as to the number of workers exposed annually.

The physical and chemical properties of DMF allow it to be widely used as a solvent in many industrial, electrolytic and petroleum processes. It is used in the manufacture of resins, polymers, acrylic fibers and synthetic leathers. Salt solutions of DMF are used in electrolytic capacitors and electroplating baths. DMF, either pure or in solution, is used to extract aromatics from petroleum mixtures. DMF also finds uses as a paint stripper and cleaner for machinery, moldings, and gas pipelines. (Ref. 5.5)

1.1.4 Physical properties (Ref. 5.4, unless otherwise stated)

CAS no.:	75-44-5
molecular weight:	73.1
appearance:	colorless liquid
odor:	faint amine-like
melting point:	-61°C
boiling point at 1 atm:	153°C
specific gravity:	0.94
vapor pressure at 20°C:	360 Pa (2.7 mm Hg)
flash point:	58°C (closed cup)
lower flammable limit:	2.2% in air by volume
molecular formula:	C_3H_7NO

odor threshold: 100 ppm
solubility: miscible with water and most common organic solvents (Ref. 5.7)
synonyms: DMF, DMFA
incompatibilities: oxidizers, alkylaluminums
molecular structure:



1.2 Limit defining parameters (The DMF air concentrations listed throughout this method are based on an air volume of 10 L and a solvent desorption volume of 1.0 mL. Air concentrations listed in ppm are referenced to 25°C and 760 mmHg.)

1.2.1 Detection limit of the analytical procedure

The detection limit of the analytical procedure is 0.16 ng/injection. This is the amount of analyte which gave a peak whose height was about 5 times the baseline noise. (Section 4.1)

1.2.2 Detection limit of the overall procedure

The detection limit of the overall procedure is 0.45 µg per sample (0.045 mg/m^3, 0.02 ppm). This is the amount of analyte spiked on the sampling device which allows recovery of an amount equivalent to the detection limit of the analytical procedure. (Section 4.2)

1.2.3 Reliable quantitation limit

The reliable quantitation limit is 0.45 µg per sample (0.045 mg/m^3 or 0.02 ppm). This is the smallest amount of analyte which can be quantitated within the requirements of a recovery of at least 75% and a precision (±1.96 SD) of ±25% or better. (Section 4.3.)

The reliable quantitation limit and detection limits reported in the method are based upon optimization of the instrument for the smallest possible amount of analyte. When the target concentration of an analyte is exceptionally higher than these limits, they may not be attainable at the routine operating parameters.

1.2.4 Instrument response to the analyte

The instrument response over the concentration range of 0.5 to 2 times the target concentration is linear. (Section 4.4)

1.2.5 Recovery

The recovery of DMF from charcoal tubes used in a 15-day storage test remained above 91% when the samples were stored at ambient temperatures. (Section 4.5) The recovery of the analyte from the collection medium during storage must be 75% or greater.

1.2.6 Precision (analytical procedure)

The pooled coefficient of variation obtained from replicate determinations of analytical standards at 0.5, 1 and 2 times the target concentration is 0.030. (Section 4.6)

1.2.7 Precision (overall procedure)

The precision at the 95% confidence level for the 15-day storage test at ambient temperature is ±14.5% (Section 4.7). This includes an additional ±5% for sampling error. The overall procedure must provide results at the target concentration that are ±25% or better at the 95% confidence level.

1.2.8 Reproducibility

Six samples spiked by liquid injection and a draft copy of this procedure were given to a chemist unassociated with the evaluation. The samples were analyzed after 1 day of storage at ambient temperature. No individual sample result deviated from its theoretical value by more than the precision reported in Section 1.2.7. (Section 4.8)

1.3 Advantages

1.3.1 The method provides high and constant desorption efficiencies at low sampler loadings.

1.3.2 The samples may be analyzed more than once if necessary.

1.3.3 The NPD is selective and sensitive.

1.4 Disadvantage

The desorbing solvent and detector may preclude the simultaneous analysis of other analytes from the charcoal tubes without additional evaluation work.

2. Sampling Procedure

2.1 Apparatus

2.1.1 Samples are collected using a personal sampling pump that can be calibrated to within ±5% of the recommended flow rate with the sampling device in line.

2.1.2 The samples are collected with 20/40 mesh coconut shell charcoal tubes, each containing a 100-mg front section and a 50-mg backup section separated by a 2-mm portion of urethane foam. Each tube contains a silanized glass wool plug ahead of the front section and a 3-mm plug of urethane foam behind the backup section. The glass tubes containing the adsorbent are 8-cm long with a 6-mm o.d. and a 4-mm i.d., and the ends are flame sealed. SKC charcoal tubes, Lot 120, were used in this evaluation.

2.2 Reagents

No sampling reagents are required.

2.3 Sampling technique

2.3.1 Open the charcoal tube immediately before sampling by breaking off the ends. The openings should be at least one half the diameter (i.d.) of the tube.

2.3.2 Connect the charcoal tube to the sampling pump with flexible tubing.

2.3.3 Place the charcoal tube in a vertical position to minimize channeling, with the backup section towards the pump.

2.3.4 Seal the charcoal tubes with plastic caps immediately after sampling. Seal each sample lengthwise with OSHA Form 21.

2.3.5 Submit at least one blank charcoal tube with each batch of samples. This charcoal tube should be subjected to exactly the same handling as the samples (break ends, seal, transport), except that no air should be drawn through it.

2.3.6 List potential interferences on the sample data sheet.

2.3.7 Transport the samples and corresponding paperwork to the lab.

2.3.8 Submit bulk samples in a separate container to prevent contamination of charcoal tube samples.

2.4 Sampler capacity

A breakthrough study was performed with a DMF test atmosphere at approximately 46 mg/m^3. The test atmosphere had a relative humidity of 68% and was at ambient temperature. A sampling rate of 1 L/min was used. The air volume sampled before 5% breakthrough occurred was 349 L. The loading on the 100-mg portion of the charcoal at this point was 16.46 mg. (Section 4.9)

2.5 Desorption efficiency

The average DE over the range of 0.5 to 2 times the target concentration is 91.7%. (Section 4.10)

2.6 Recommended air volume and sampling rate

2.6.1 The recommended air volume is 10 L and the recommended sampling rate is 0.2 L/min.

2.6.2 Although breakthrough data indicate a large air volume can be sampled, a 10-L air volume was recommended as it is a typical air volume for solvents, and would circumvent any collection problems associated with an interference saturating the charcoal.

2.6.3 When short-term (15 min) samples are required the recommended sampling rate is 0.2 L/min. The reliable quantitation limit (0.45 µg/sample) is equivalent to 0.05 ppm (0.15 mg/m^3) for a short-term sample.

2.7 Interferences (sampling)

Suspected interferences should be reported to the laboratory with submitted samples.

2.8 Safety precautions

2.8.1 Wear eye protection when breaking off the ends of the charcoal tubes.

2.8.2 Position the sampling device on the worker so as not to interfere with his/her work or safety.

2.8.3 Observe all safety regulations of the area in which sampling is performed.

3. Analytical Procedure

3.1 Apparatus

3.1.1 A gas chromatograph (GC) equipped with a nitrogen/phosphorus detector (NPD). A Hewlett-Packard 5840A GC fitted with an NPD was used in this evaluation. Injections were performed using a Hewlett-Packard 7671A automatic sampler.

3.1.2 A GC column capable of separating the DMF from the solvent, the internal standard and any listed interferences. A 6-ft × 2-mm i.d. glass column packed with 80/100 mesh Chromosorb 101 was used in this evaluation.

3.1.3 An electronic integrator or other suitable means of measuring detector response. A Hewlett-Packard 5840 GC Terminal was used in this evaluation.

3.1.4 Two-milliliter vials with Teflon-lined caps were used for sample desorption and standard preparation.

3.2 Reagents

3.2.1 DMF, reagent grade.

3.2.2 Acetone, reagent grade.

3.2.3 Propionitrile, reagent grade.

3.2.4 Desorbing solution: Acetone containing 1 µL/mL propionitrile was used in this evaluation.

3.2.5 Hydrogen, GC grade.

3.2.6 Air, GC grade.

3.2.7 Helium or nitrogen, GC grade.

3.3 Standard preparation

Prepare DMF standards in the desorbing solution. Standards should be prepared in the range of from 0.015 to 0.3 µL/mL when sample air volumes are 10 L. Sample concentrations should be bracketed with standards because of possible non-linearity of the NPD.

3.4 Sample preparation

3.4.1 Place the 100-mg portion of charcoal in one vial and the 50-mg portion in a second vial. Discard the glass wool and the urethane plugs.

3.4.2 Dispense 1.0 mL of the desorbing solution into each vial.

3.4.3 Immediately seal the vials with Teflon-lined caps and allow them to desorb for 1 h. Shake the vials by hand several times during the desorption period.

3.5 Analysis

3.5.1 GC conditions

column temperature:	170°C
injector temperature:	200°C
detector temperature:	250°C
nitrogen flow rate:	26 mL/min
hydrogen flow rate:	3 mL/min
air flow rate:	65 mL/min
injection volume:	0.40 µL
retention time:	6.20 min

3.5.2 Chromatogram See Figure 4.

3.5.3 An internal standard calibration method is preferable, since it corrects for injection size and slight changes in the NPD response.

3.5.4 Use a suitable method to measure detector response, such as electronic integration.

3.5.5 Bracket sample concentrations with standards.

3.6 Interferences

3.6.1 Any compound having a similar retention time as DMF or the internal standard which gives an NPD response is a potential interference.

3.6.2 GC parameters (temperature, column, etc.) may be changed to circumvent interferences.

3.7 Calculations

3.7.1 Prepare a calibration curve from the analytical standards by plotting detector response versus the analytical standard concentrations (in µg/mL).

3.7.2 Determine the concentration of DMF in the samples by using the calibration curve.

3.7.3 Add the amount of DMF found in the backup section of the tube to that found in the front section and subtract the amount found in the blank. The air concentration of DMF may then be calculated using the following equation:

$$mg/m^3 = (A)(B)/(C)(D)$$

where A is µg DMF/mL desorption solvent
B is desorption volume (1 mL)
C is sample air volume (L)
D is desorption efficiency (decimal form)

The air concentration may also be expressed in ppm by volume at 760 mmHg and 25°C with the following equation:

$$ppm = (E)(F)/(G)$$

where E is DMF concentration in mg/m^3
F is 24.46, the molar volume of an ideal gas at 760 mmHg and 25°C
G is 73.10, the molecular weight of DMF

3.8 Safety precautions

3.8.1 Avoid skin contact and inhalation of all chemicals.

3.8.2 Restrict the use of all chemicals to a fume hood.

3.8.3 Wear safety glasses and a lab coat in all laboratory areas.

4. Backup Data

4.1 Detection limit of the analytical procedure

The detection limit of the analytical procedure was determined by injecting 0.40 µL of an analytical standard of 0.40 µg/mL (0.40 µg/mL x 0.40 µL = 0.16 ng/injection). This gave a peak whose height was approximately five times the baseline noise (Figure 4.1).

4.2 Detection limit of the overall procedure

The detection limit of the overall procedure is 0.45 µg/sample (0.045 mg/m^3 or 0.02 ppm). This is the amount of DMF which, when spiked on the sampling device, will allow recovery of an amount approximately equivalent to the detection limit of the analytical procedure (0.16 ng/injection or 0.40 µg/sample).

Table 4.2
Data for Detection Limit of the Overall Procedure

sample no.	theoretical amount (µg)	amount recovered (µg)
1	0.4528	0.4528
2	0.4528	0.4057
3	0.4528	0.4333
4	0.4528	0.4664
5	0.4528	0.4338
6	0.4528	0.4247

4.3 Reliable quantitation limit

The reliable quantitation limit is that amount of DMF which, when spiked onto the sampling device, will allow recovery of at least 75% and have a precision (1.96 SD) of ±25% or better. The reliable quantitation limit is the same as the detection limit of the overall procedure in this evaluation (using the recommended injection size of 0.40 µL). The front sections of six SKC Lot 120 charcoal tubes were spiked with 8 µL of a 56.6 µg/mL solution of DMF in acetone, and stored in a laboratory refrigerator overnight. The tubes were desorbed with 1.0 mL of acetone containing 1 µL/mL propionitrile as an internal standard and analyzed.

Table 4.3
Data for Reliable Quantitation Limit
(Based on samples and data of Table 4.2)

percent recovered	statistics
100	
89.6	mean = 96.3
95.7	SD = 4.7
103	Precision = (1.96)(±4.7)
95.8	= ±9.2
93.8	

4.4 Instrument response to the analyte

The instrument response to the analyte over the range of 0.5 to 2 times the PEL is linear with a sensitivity of 3800 area counts per (µg/mL). (Table 4.4, Figure. 4.4)

Table 4.4
DMF Sensitivity Data

× target concn µg/mL	0.5× 142	1.0× 283	2.0× 566
area counts	458500	1104000	2114000
	469400	1105000	2130000
	482500	1105000	2140000
	497300	1100000	2150000
	507800	1103000	2159000
	514200		2159000
mean	488283	1103400	2142000

4.5 Storage Data

Thirty-three charcoal tubes were liquid spiked with a loading equivalent to the PEL based on a 10-L air volume. Three tubes were desorbed and analyzed immediately. Of the remaining thirty tubes, fifteen were refrigerated at -5°C and fifteen were stored at ambient temperature in a laboratory drawer. Approximately every three days, three tubes from the refrigerated group and three from the ambient group were desorbed and analyzed. The recovery of DMF from charcoal, as determined from a best fit curve, remained above 91% during the sixteen

day storage test. No appreciable difference was observed between the refrigerated and the ambient samples (Table 4.5.1, Figures 4.5.1 and 4.5.2).

Table 4.5.1
Storage Study of Liquid Spiked Samples

time (days)	percent recovery (ambient)			percent recovery (refrigerated)		
0	93.2	90.9	96.4	93.2	90.9	96.4
4	92.4	92.4	93.0	91.0	95.1	93.6
6	91.2	91.9	91.2	92.2	92.2	85.0
9	89.2	91.1	93.3	89.3	99.7	94.7
13	89.6	90.9	90.9	89.0	94.7	92.4
16	92.7	91.6	92.7	84.0	89.7	86.1

Storage samples were also collected from a dynamically generated atmosphere of DMF at 71% relative humidity and 23°C. Thirty-six charcoal tubes were used to sample this atmosphere. Ten-liter air samples were taken at a rate of 0.2 L/min. Six samples were desorbed and analyzed immediately; these represent day-zero storage. The remaining thirty were divided into two groups of fifteen; one group was stored under refrigeration at -5°C and the other at ambient temperature in a laboratory drawer. The samples from each group were analyzed so as to provide storage data at 3-day intervals for a period of fifteen days. Front and back sections of each tube were analyzed separately.

Analysis of six vapor-generated samples on day zero yielded a recovery of 65%, rather than 92% which would have been expected if the only bias present was the desorption efficiency. The additional bias was attributed to DMF loss in the vapor generating system; NIOSH reported a similar finding (Ref. 5.8). Therefore the theoretical concentration of the DMF test atmosphere was considered to be approximately 70% of the PEL. Since the day-zero samples would show only the effects of desorption efficiency and not storage, the normalized results were adjusted to reflect only the loss due to desorption on day zero. This was accomplished by multiplying the actual storage recoveries by 1.41 (91.7/65). These storage results, which are comparable to the storage results obtained with liquid-spiked samples, indicate no significant bias that could be attributed to storage instability (Table 4.5.2, Figures 4.5.3 and 4.5.4).

The precision of the overall procedure must be ±25% or better at the 95% confidence level for samples collected at the target concentration. The precision at the 95% confidence level for the 15-day storage test at ambient temperature (Figure 4.5.4) is ±14.5%. This includes an additional ±5% for sampling error.

Table 4.5.2
Storage Study - Vapor Generated Samples

time (days)	percent recovery (ambient)			percent recovery (refrigerated)		
0	94	95	93	94	95	93
	90	93	91	90	93	91
3	95	–	93	99	108	–
6	97	97	97	99	99	98
9	85	77	90	94	94	91
12	97	94	95	101	104	101
15	95	--	95	116	99	99

4.6 Precision (analytical method only)

The precision of the analytical procedure is defined as the pooled coefficient of variation determined from replicate injections of analytical standards at 0.5, 1 and 2 times the target concentration. Based on the data of Table 4.4, coefficients of variation (CV) for the three levels and the pooled coefficient of variation (CVp) are given in Table 4.6.

Table 4.6
Precision of the Analytical Method
(Based on the Data of Table 4.4)

× target concn µg/sample	0.5× 142	1.0× 283	2.0× 566
SD[1]	21960	2074	17740
CV	0.0450	0.0019	0.0083
CVp	0.027		

1 - in area counts

4.7 Precision (overall procedure)

The precision of the overall procedure is determined from the storage data. The determination of the standard error of estimate for a regression line plotted through the graphed storage data, as in Figure 4.5.4, allows the inclusion of storage time as one of the factors affecting overall precision.

The standard error of estimate (SEE) is similar to the standard deviation, except it is a measure of dispersion of data about a regression line instead of about a mean. It is determined with the following equation:

$$SEE = \sqrt{\frac{\sum (Y_{obs} - Y_{est})^2}{n-k}}$$

where n is total number of data points
k is 2 for linear regression
k is 3 for quadratic regression
Y_{obs} is observed percent recovery at a given time
Y_{est} is estimated percent recovery from the regression line at the same given time

An additional 5% for pump error is added to the standard error of estimate by the addition of variances. The precision at the 95% confidence level is obtained by multiplying the standard error of estimate (with pump error included) by 1.96 (the z-statistic from the standard normal distribution at the 95% confidence level). The 95% confidence intervals are drawn about their respective regression lines in the storage graphs.

4.8 Reproducibility

Six liquid-spiked samples and a draft copy of this procedure were given to a chemist unassociated with this evaluation. The samples were analyzed after 1 day of storage at ambient temperature.

Table 4.8
DMF Reproducibility

theoretical amount (µg)	amount found (µg)	% found	% deviation
302.2	294.0	97.3	-2.7
234.2	235.3	100.5	+0.5
136.0	134.7	99.0	-1.0
302.2	295.5	97.8	-2.2
136.0	127.6	93.8	-6.2
234.2	225.6	96.3	-3.7

Precision of the overall procedure (from Section 1.2.7) is ±14.5%. DE for charcoal = 91.7%

4.9 Sampler Capacity

Analyte breakthrough in this evaluation was determined by sampling a dynamically generated test atmosphere at approximately twice the target level using only the front section of the sorbent tube.

Breakthrough is defined as the point at which the concentration of DMF in the atmosphere which has passed through the sorbent tube is 5% of the upstream concentration of the test atmosphere.

This initial study using the vapor generator indicated a discrepancy between the theoretical concentration of DMF and the experimentally determined concentration. This discrepancy was found when a charcoal tube that had been used to sample the atmosphere was analyzed. The experimentally determined concentration was only 70% of the theoretical concentration (Table 4.9.1). As previously stated in Section 4.5, NIOSH mentions this type of problem in the backup data report for their dimethylformamide method (Ref. 5.8). A further discussion of this is given in Section 4.11.

Table 4.9.1
Analysis of Charcoal Tube

theor. concn (mg/m^3)	air vol (L)	expected (mg)	recovered (mg)	DE corr.	% recovered
61.05	255.9	15.62	10.10	11.00	70

Before proceeding with the evaluation on charcoal, the effect of humidity on the capacity of the standard size silica gel tube was determined. The NIOSH method, which uses the silica gel tube, did not address the effects of humidity. The concentration of the test atmosphere was 46.22 mg/m^3 as determined by the analysis of the front portion of a silica gel tube. Breakthrough was monitored downstream from the sampling tube with a gas chromatograph equipped with a gas sampling valve. DMF was introduced into the vapor generation system through a heated inlet at a rate of 9.36 mg/min. The test atmosphere was sampled at a rate of 1 L/min and an average relative humidity of 67% at 23°C.

The results of two capacity studies on silica gel yielded an average 5% breakthrough volume of 159 L. The capacity of silica gel for DMF is 7.36 mg (Table 4.9.2, Figure 4.9.2). Examination of the capacity data indicates that silica gel is an adequate solid sorbent for collection of DMF even at the studied humidity.

Table 4.9.2
DMF Breakthrough with Silica Gel

test	5% breakthrough volume (L)	capacity (mg)
1	164.4	7.46
2	154.2	7.25
$\bar{x}$	159.3	7.36

The capacity of SKC, Inc. Lot 120 charcoal was tested using the same vapor generation system and delivery rate as in the silica gel studies. The concentration of the test atmosphere, generated at 68% relative humidity and 25°C, was found to be 46.56 mg/m^3 as determined by the analysis of the front portion of a charcoal tube. At a sampling rate of 1 L/min the 5% breakthrough volume was found to be 349 L and the capacity of the charcoal for DMF 16.46 mg (Table 4.9.3, Figure 4.9.3). Only one capacity study was performed since the breakthrough volume greatly exceeded the commonly used air volume of 10 L for charcoal. The capacity study indicates that charcoal is an effective collection medium for DMF.

Table 4.9.3
DMF Breakthrough with Charcoal

test	5% breakthrough volume (L)	capacity (mg)
1	349.0	16.46

4.10 Desorption efficiency

The desorption efficiency was determined at 0.5, 1 and 2 times the target concentration by injecting known amounts of solutions containing DMF in acetone onto the 100-mg portion of charcoal tubes. Six tubes at both the 0.5 and 2 times the PEL level were prepared. Seven tubes were prepared at the PEL level. All tubes were capped and allowed to equilibrate overnight under refrigeration. The tubes were desorbed with 1.0 mL of acetone and analyzed.

Desorption efficiencies at 0.1, 0.05 and 0.02 times the target concentration were also determined to ensure that the desorption was constant at lower analyte concentrations. Charcoal tubes at each of the three levels were prepared by injecting known amounts of DMF in acetone onto the 100-mg portion of the tubes. All tubes were capped and allowed to equilibrate overnight under refrigeration. The tubes were then desorbed and analyzed.

Table 4.10
Desorption Efficiency of DMF from Charcoal

0.5× target concn 142 µg spiked		1× target concn 283 µg spiked		2× target concn 566 µg spiked		0.1× target concn 28.3 µg spiked		0.05× target concn 14.2 µg spiked		0.02× target concn 5.66 µg spiked	
µg found	DE (%)	µg found	DE (%)	µg found	DE (%)	µg found	DE (%)	µg found	DE (%)	µg found	DE (%)
133	93.7	249	88.0	530	93.6	24.4	86.2	12.4	87.3	5.49	96.9
133	93.7	249	88.0	528	93.3	24.6	86.9	12.5	88.0	5.48.5.2	96.8
133	93.7	261	92.2	526	92.9	24.6	86.9	12.73	89.4	1	92.0
131	92.2	254	89.7	524	92.6	24.8	87.6	12.4	87.3	5.57	98.4
128	90.1	260	91.9	510	90.1	24.8	87.6	12.8	90.1	5.37	94.9
132	93.0	252	89.0	514	90.8	28.0	98.9	11.4	80.3	5.12	90.4
		260	91.9			25.0	88.3	12.5	88.0	4.90	86.6
						27.4	96.8	11.8	83.1	4.53	80.0
						26.0	91.9	11.7	82.4	4.59	81.1
								11.4	80.3	5.98	106
					average						
132	92.7	255	90.1	522	92.2	25.5	90.1	12.2	85.6	5.22	92.3

Average DE over range 0.5× to 2× target concn is 91.7%. Average DE over range 0.1× to 0.02× target concn is 89.3%.

4.11 Loss of DMF in the vapor generating system

A number of tests were performed to determine if the loss of DMF in the vapor generating system was due to sampling technique.

The syringe pump which was used to meter DMF into the vapor generating system was recalibrated. Initial and final calibrations were within 1%.

The calibration of the dilution air rotameters was checked and found to be accurate.

The glass-wool plug and the foam plug separating the front and back sections of a vapor-spiked charcoal tube were each desorbed and analyzed to check for DMF adsorption. DMF was found in neither.

In order to determine if collection on charcoal was the problem, two sets of side-by-side samples utilizing silica gel sorbent tubes and methanol bubblers, in addition to charcoal, were collected. The test atmosphere theoretically contained 30 mg/m^3 DMF in dry air. Samples were collected at approximately 1 L/min for 50 min. Results from the analysis of the side-by-side samples indicated the concentration of the test atmosphere to be 12-23% lower than the theoretical value (Table

4.11.1). The results show that the discrepancy between the theoretical concentration and the observed concentration is not unique to sampling with charcoal.

Table 4.11.1
Three Collection Media at 30.21 mg/m^3

media	test	air vol (L)	expected (µg)	recovered (µg)	DE corr. (µg)	% recovery
charcoal	1	48.8	1473	1046	1139	77
bubbler	1	44.4	1341	1076	1076	80
silica gel	1	52.0	1571	874	1053	67
charcoal	2	48.4	1462	1187	1293	88
bubbler	2	46.5	1405	1212	1212	86
silica gel	2	51.2	1547	973	1172	76

DE for charcoal = 91.7%. DE for silica gel = 83.0%.

In order to determine if DMF losses in the vapor generating system were constant or concentration dependent, DMF test atmospheres at theoretical test concentrations of twice and ten times the PEL were studied. Three charcoal tubes were collected at a rate of 0.2 L/min for 25 min from a dry test atmosphere which was theoretically 10 times the PEL. These tubes were analyzed and the results compared with the data of Table 4.9.1 which was collected at twice the PEL. This comparison is shown in Table 4.11.2 and indicates that at both twice and ten times the PEL the recovery is about 70%. Therefore the loss does not appear to be concentration dependent. This work also indicated that pacification of the vapor generating system with high DMF concentrations prior to use would not alleviate the loss of DMF.

Table 4.11.2
Concentration Effects

theor. concn (mg/m^3)	air vol (L)	expected (mg)	recovered (mg)	DE corr. (mg)	% recovery
61.05	255.9	15.62	10.10	10.98	70
318.0	5.26	1.673	1.060	1.152	69
318.0	4.96	1.577	0.993	1.079	68
318.0	5.21	1.657	1.121	1.218	74

DE for charcoal = 91.7%.

Humidity was not the cause of low results. Samples collected under both dry-air conditions (represented by the charcoal tubes in side-by-side sampling, Table 4.11.1) and humid air conditions (represented by the vapor-spiked storage samples, Section 4.5) gave results lower than the theoretical concentrations.

In conclusion, the reason for the discrepancy between the theoretical concentrations of DMF in the vapor generating system and experimentally determined concentrations could not be attributed to any of the parameters tested, including the sampling technique.

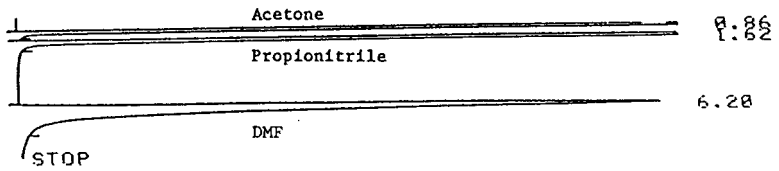


Figure 4. Chromatogram of DMF. (283 µg/mL) For GC conditions see Section 3.5.1.

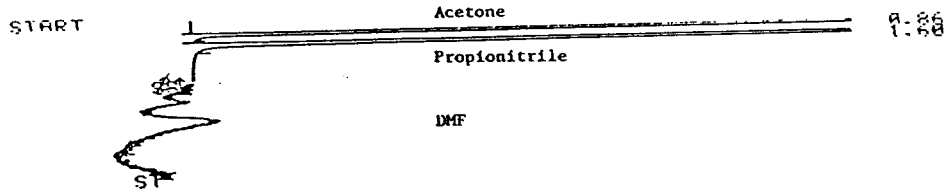


Figure 4.1. Chromatogram of DMF at the detection limit of the analytic procedure. (0.16 ng DMF per injection).

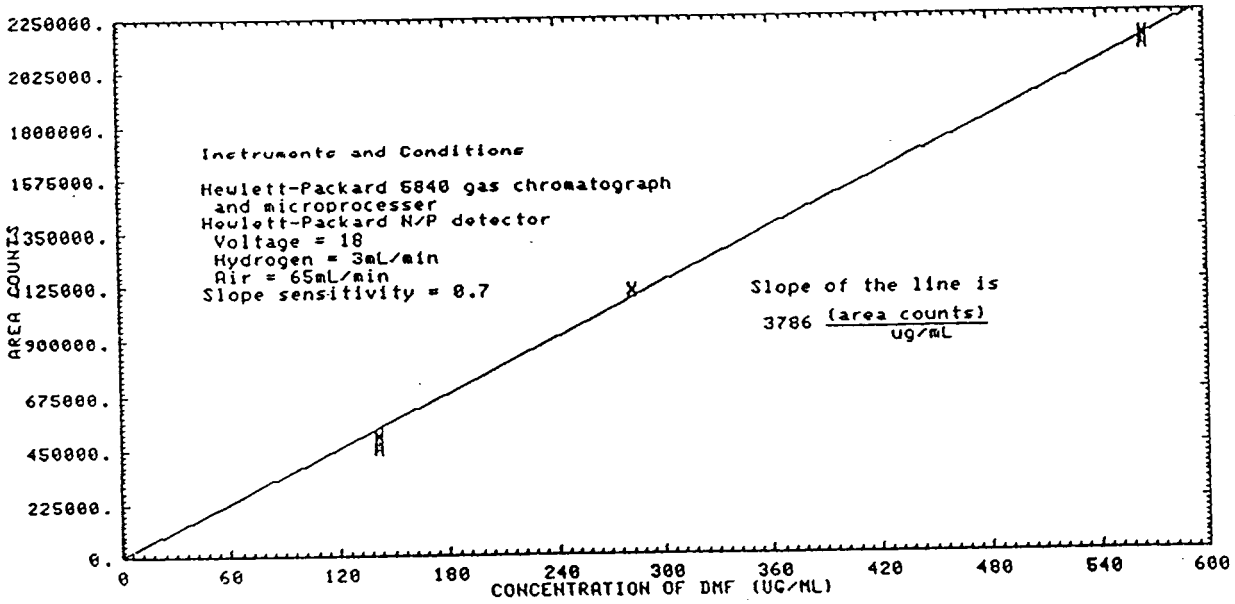


Figure 4.4. Instrument response to DMF.

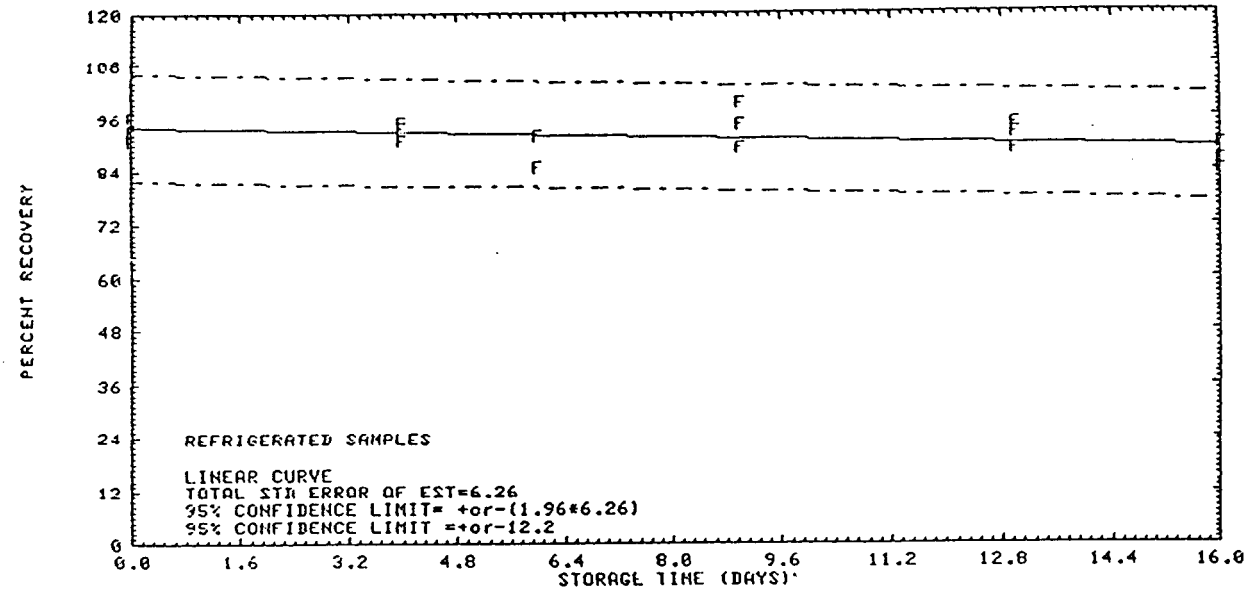


Figure 4.5.1. Storage test at reduced temperature with liquid-spiked samples.

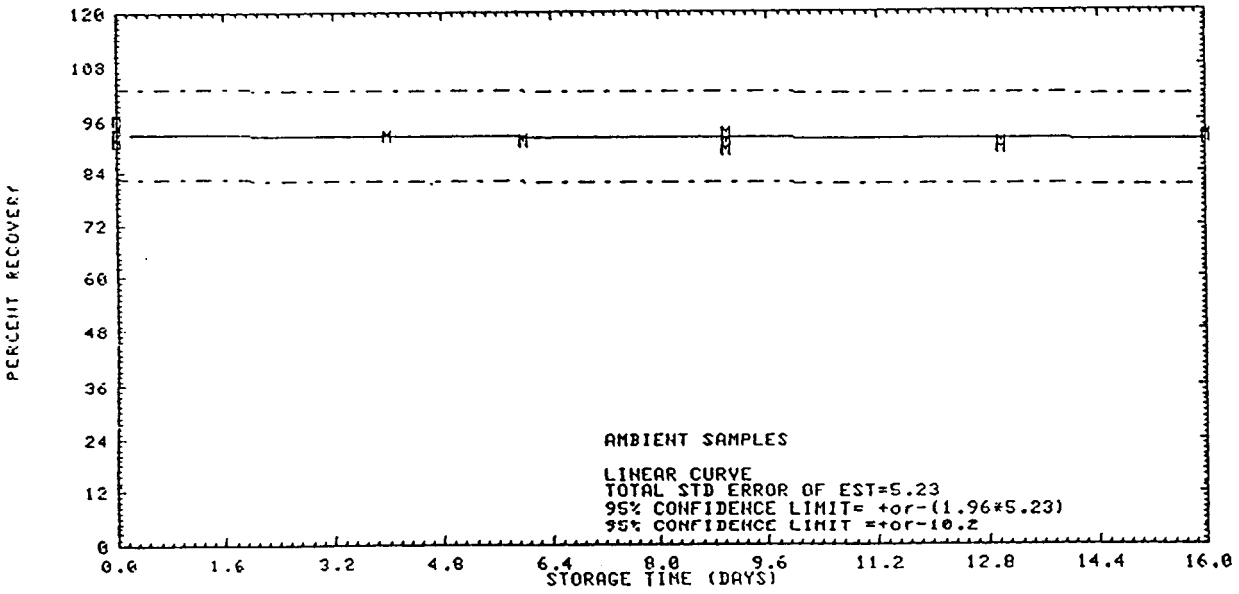


Figure 4.5.2. Storage test at ambient temperature with liquid-spiked samples.

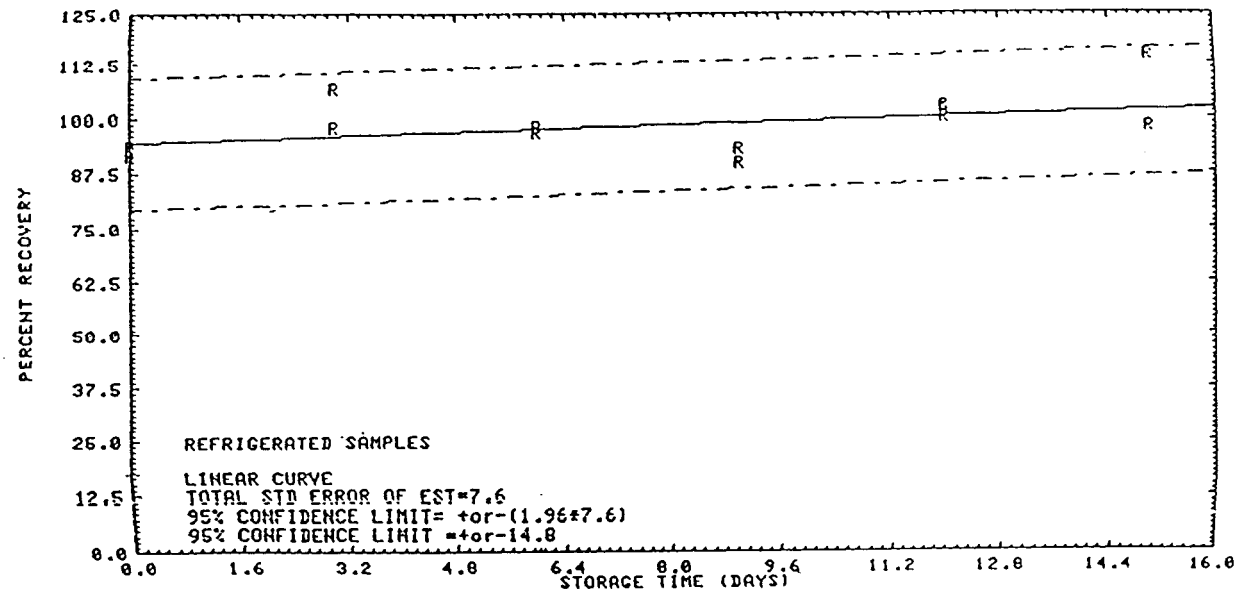


Figure 4.5-3. Storage test at reduced temperature with samples collected from test atmosphere.

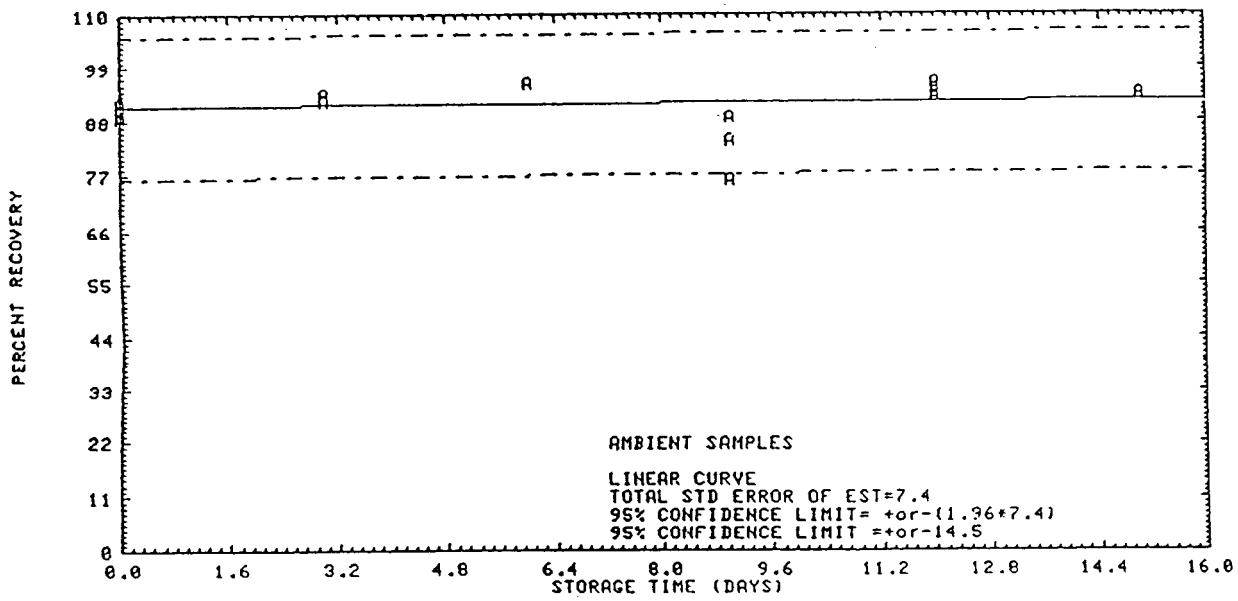


Figure 4.5.4. Storage test at ambient temperature with samples collected from test atmosphere.

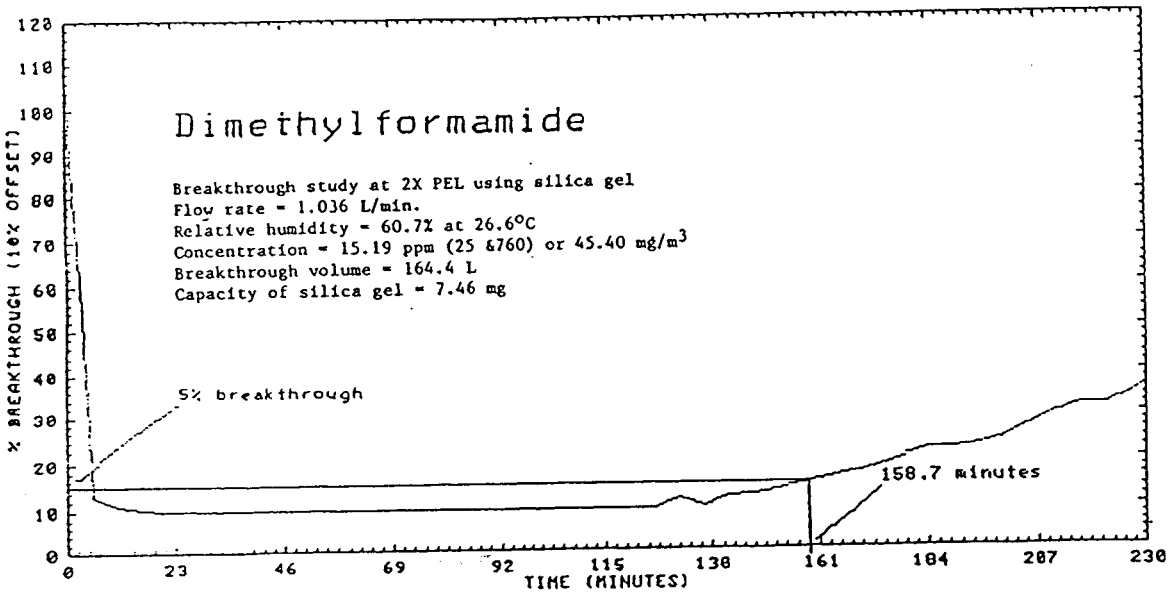


Figure 4.9.2 Breakthrough study of DMF with silica gel tube.

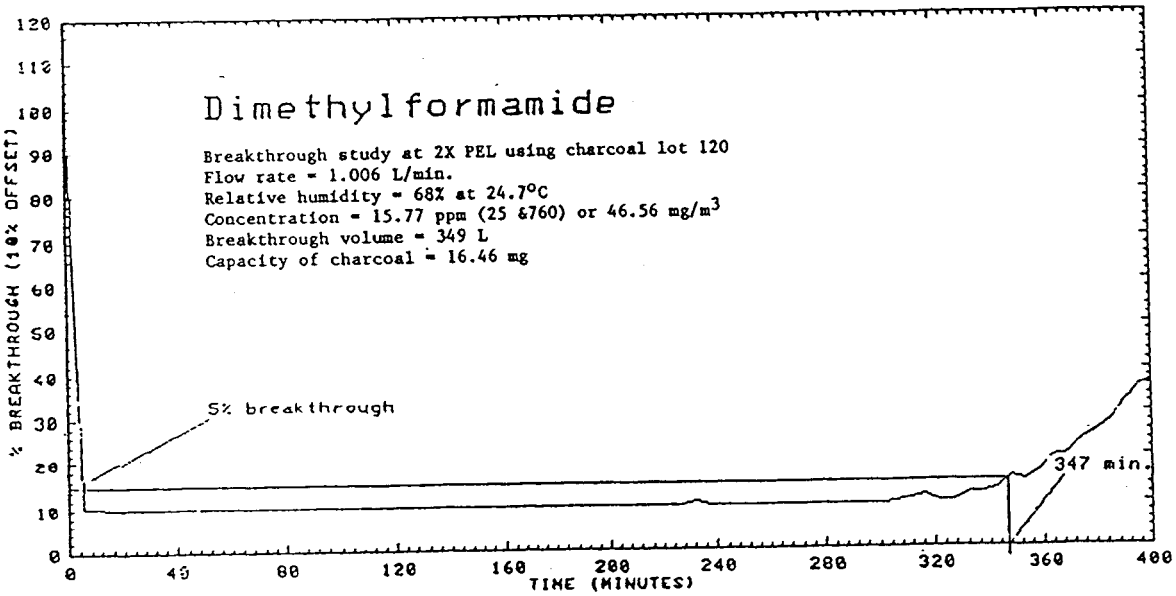


Figure 4.9.3 Breakthrough study of DMF with charcoal tube.

5. References

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