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# A method for sampling and analysis of 2-nitropropane in air

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**The development of a method for sampling and analysis of airborne 2-nitropropane is described. The 5% breakthrough volumes of several sorbents for the analyte were determined using a challenge atmosphere of 10 ppm (36 mg/m$^3$) 2-nitropropane in humid air at a flow-rate of 0.2 liter/minute. Chromosorb 106 (60/80 mesh), a cross-linked polystyrene porous polymer, had the highest capacity - 10.4 liters. Samples collected on Chromosorb 106 were desorbed with ethyl acetate and analyzed by gas chromatography using a flame ionization detector. Recovery was quantitative at or above the 10 μg/sample level. The precision of analysis was 0.05 relative standard deviation for eighteen 3-L samples of 2-nitropropane taken from humid atmospheres over the range 1.0-10 ppm (3.6-36 mg/m$^3$).**

# A method for sampling and analysis of 2-nitropropane in air

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## introduction

2-Nitropropane is a solvent which is widely used in the production of vinyl and epoxy coatings and printing inks. NIOSH estimates that as many as 100 000 workers may be exposed to this material nationwide. An inhalation study, sponsored by NIOSH, indicated that all laboratory rats exposed to 207 ppm (745 mg/m$^3$) of 2-nitropropane for six months developed hepatocellular carcinoma or hepatic adenoma.[1] Although the carcinogenic potential to man has not been established, the need to monitor human exposure to this material is apparent.

Previous research had indicated that gas chromatographic analysis of 2-nitropropane was straightforward; however, the analyte decomposed when stored on petroleum-based charcoal.[2] Therefore, it was necessary to evaluate other materials for collection and storage of 2-nitropropane. These included Florisil, silica gel and several porous polymers.

A method for monitoring exposure to 2-nitropropane in air is described in this paper. It involves collection of the analyte on Chromosorb 106, desorption with ethyl acetate and analysis via gas chromatography using a flame ionization detector.

## experimental

### *apparatus*

#### chromatograph

A Packard Model 427 gas chromatograph, equipped with a flame ionization detector, was used for the analysis of all samples. The column was 6.1 m × 4 mm i.d. stainless steel tubing packed with 10% FFAP on 80/100 mesh Chromosorb W-AW (Supelco). Chromatogram peak areas were integrated by a Hewlett-Packard 3352 Laboratory Data System interfaced to the chromatograph via an analog-to-digital signal converter.

#### sorbents

The Chromosorb Century Series porous polymers used in this study are marketed by Johns-Manville Co. (Denver, Colorado). In order to remove contaminants which interfered with the analysis, these sorbents were refluxed

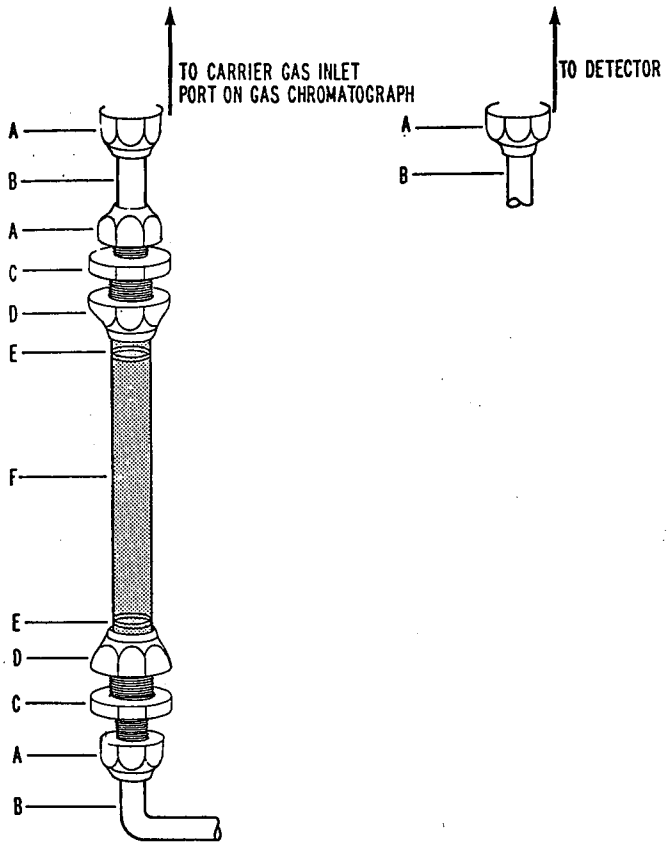


Figure 1 – Batch drying apparatus for porous polymers.

A. 1/4" Swagelock fittings
B. 1/4" Copper tubing
C. 1/4" to 1/2" Swagelock adaptor
D. 1/2" Swagelock fitting with Teflon ferrule
E. Silanized glass wool plugs
F. 6" × 1/2" O.D. glass drying tube

Disclaimer: Mention of products or trade names does not constitute endorsement by the U.S. Government Public Health Service.

**TABLE I**
**Breakthrough Volumes for 100 mg Beds of Twelve Solid Sorbents Challenged at 200 $cm^3/min$ with 36 $mg/m^3$ (10 ppm) 2-Nitropropane in Humid Air**

| Sorbent | Mesh Size | Surface Area ($m^3/gm$)[3] | Pressure Drop (torr) | % Relative Humidity | 5% Breakthrough Volumes (liters)[A] |
|---|---|---|---|---|---|
| Silica | 20/40 | --- | --- | 85 | 0.4 |
| Florisil | 30/48 | --- | --- | 62 | 0.4 |
| XAD-2 | 16/50 | 350 | 1.0 | 85 | 0.6 |
| Porapak N | 50/80 | --- | 9.8 | 76 | 2.5 |
| Porapak Q | 50/80 | 634 | 12.8 | 76 | 4.1 |
| Chromosorb 102 | 60/80 | 200-400 | 10.5 | 82 | 1.6 |
| Chromosorb 103 | 60/80 | 15-25 | 9.7 | 82 | 0.4 |
| Chromosorb 104 | 60/80 | 100-200 | 9.8 | 76 | 3.4 |
| Chromosorb 105 | 60/80 | 600-700 | 10.4 | 84 | 5.5 |
| Chromosorb 106 | 20/40 | 700-800 | 1.0 | 87 | 2.7 |
| Chromosorb 106 | 60/80 | 700-800 | 11.8 | 83 | 10.4 |
| Chromosorb 107 | 60/80 | 400-500 | 8.5 | 84 | 3.4 |

--- information not available

[A]Volume passed through sorbent bed when effluent concentration reached 5% of the challenge concentration.

with acetone in a Soxhlet apparatus for two hours and dried by purging with helium for one hour in the batch apparatus shown in Figure 1. The XAD-2 resin, manufactured by Rohm and Haas Company, (Philadelphia, Pa.) was supplied by A. D. Little Co. (Cambridge, Mass.). It had been pre-extracted with several solvents and was used as obtained. Florisil, obtained from MCB Chemicals (Norwood, Ohio), was deactivated by the addition of water (3% w/w). The silica gel was supplied by SKC Corporation (Pittsburgh, Pa.), and was used as received.

### collection tubes

For breakthrough experiments, 100-mg beds of each sorbent listed in Table I were packed into 4-mm i.d. glass

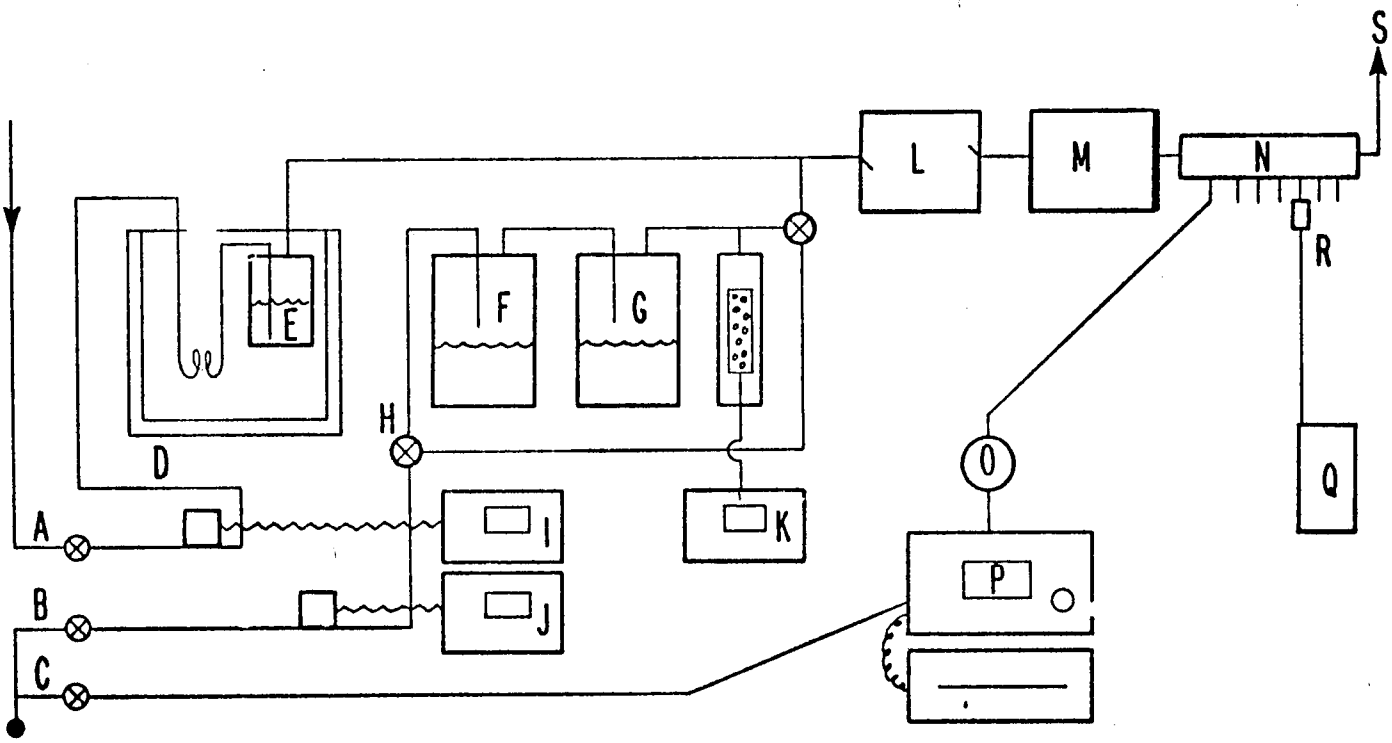


Figure 2 – 2-Nitropropane generation and sampling system.

A. Air supply to contaminant reservoir
B. Dilution air line
C. Air supply to hydrocarbon analyzer
D. Constant temperature bath
E. 2-Nitropropane reservoir
F. and G. Water containers for humidifying dilution air
H. Bypass line
I. and J. Mass flowmeters
K. Relative humidity sensor
L. and M. Mixing chambers
N. Sampling manifold
O. Vacuum pump
P. Total hydrocarbon analyzer with strip chart recorder
Q. Sampling pump
R. Sampling tube
S. Vent

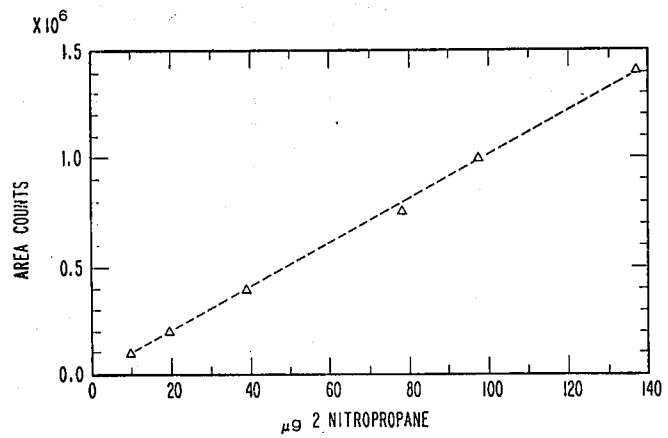


Figure 3 — Calibration curve.

μg 2-Nitropropane in 1.0 mL ethyl acetate
Δ Experimental points
--- Linear least squares line

tubing, 7 cm in length. The sorbents were held in place by small plugs of silanized glass wool.

Sampling was conducted using the same dimension glass tubes packed with 100-mg front and 50-mg backup sections of acetone-washed Chromosorb 106. The two sections were separated by a 2-mm plug of polyurethane foam. A plug of silanized glass wool was placed just before the front section, another urethane plug was placed at the outlet. The tubes were flame-sealed at both ends for storage before use.

### solvents and standards

2-Nitropropane, 97%, was obtained from Fisher Chemical Co. (Pittsburgh, Pa.). Ethyl acetate, distilled-in-glass grade, was obtained from Burdick and Jackson Co. (Muskegon, Mich.). Chromato-quality acetone was obtained from MCB Chemicals (Norwood, Ohio).

### generation system

Figure 2 shows the generation system. Test atmospheres of 2-nitropropane in humid air (relative humidity ~ 80%) were generated dynamically by passing clean dry air (from line A) at 10-20 $cm^3$/min through a fritted bubbler (E) containing liquid 2-nitropropane maintained at 4 °C in a constant temperature bath (D). The vapor then was carried to mixing chambers (L, M), where dilution air (from line B) was added at 7500 $cm^3$/min., and finally to a seven-port sampling manifold (N) which was vented to an exhaust hood (S). The dilution air was humidified by passing it over water in two containers (F, G), that were placed serially in line immediately before the mixing chamber. The flowrates of the contaminant stream and dilution air were monitored with mass flow meters (I, J) (Hastings Raydist, Hampton, Va.). The temperature and relative humidity of the dilution air were monitored with an electronic hygrosensor (K) (Humitemp, Phys-Chem Research Corp., New York, N.Y.) placed downstream of the water containers. All components of the generation system were constructed of glass or polyfluoroethylene.

The generator output was monitored by passing the sample atmosphere from one port, through a rotating piston pump (O) at 200 $cm^3$/min into a Beckman Model 400 total hydrocarbon analyzer (P) (Beckman Instruments Co., Fullerton, Ca.) connected to a strip chart recorder. The detector was calibrated over the range 1.1-11 ppm (4.0-40 mg/$m^3$) with 2-nitropropane in dry air atmospheres. These were prepared by mixing the analyte with dry air in polyvinylfluoride (PVF) bags fitted with a toggle valve and septa. Personal sampling pumps (Q), calibrated with each tube (R) in line, were used for collection of all samples.

## *procedure*

### breakthrough studies

In order to determine the capacities of various materials for 2-nitropropane, a tube containing 100 mg of the sorbent of interest was placed in the sampling line of the total hydrocarbon analyzer and challenged at 200 $cm^3$/min with 36 mg/$m^3$ (10 ppm) 2-nitropropane in humid air. Breakthrough was determined by monitoring the pump effluent with the total hydrocarbon analyzer. Table I lists the sorbents studied, some pertinent physical properties and the breakthrough volumes determined for each.

### analytical method

All samples were desorbed in 1.0 mL of ethyl acetate for at least 30 minutes. A 5-μL aliquot (1-μL solvent flush) of the

**TABLE II**
**Recovery of 2-Nitropropane from Chromosorb 106 after Storage for 1 and 15 Days[A]**

| Nominal Level (μg) | Amount Recovered (%) and 95% Confidence Limits | |
|---|---|---|
| | Day 1 | Day 15 |
| 98 | 98 ± 3.3 | 98 ± 3.1 |
| 49 | 100 ± 3.1 | --- |
| 9.8 | 101 ± 2.4 | 99 ± 13 |
| 0.98 | 105 ± 16 | 83 ± 31 |

[A]Six replicate samples for each set of analyses. Samples were prepared by adding measured amounts of 2-nitropropane in ethyl acetate to the sorbent.

**TABLE III**
**Comparison of 2-Nitropropane in Humid Air Concentrations Determined by Total Hydrocarbon Analyzer and Sorbent Sampling - G.C. Method[A]**

| Total Hydrocarbon Analyzer | Gas Chromatographic Method[B,C,D] |
|---|---|
| 31.0 | 28.3 ± 1.3 |
| 14.0 | 14.9 ± 0.6 |
| 3.3 | 3.1 ± 0.2 |

[A]concentrations in mg/$m^3$

[B]includes 95% confidence limits

[C]six replicate samples for each set of analyses; 3-liter test atmosphere

[D]includes analysis of backup sections; no 2-nitropropane was found on them

**TABLE IV**
**Stability of 2-Nitropropane Samples Collected from Humid Air onto Chromosorb 106[A]**

| Day Analyzed | Mean Concentration ($mg/m^3$) and 95% Confidence Limits[B] |
|---|---|
| 1 | 4.6 ± 0.7 |
| 7 | 4.9 ± 0.4 |
| 14 | 5.0 ± 0.7 |
| 28 | 4.8 ± 0.2 |

[A]six replicates for each set of analyses; 3-L test atmosphere

[B]mean differences are not significant at the 95% level of confidence - the backup sections of all collected samples were analyzed; none of the analyte was found on them

sample was injected into the chromatograph. The temperatures of the column, injector port and detector zone were maintained at 90 °C, 190 °C and 200 °C respectively. Typical gas flow rates were: Air 339 $cm^3/min$, hydrogen 33 $cm^3/min$ and helium 20 $cm^3/min$.

Under these conditions, the analyte eluted in approximately 20 minutes on the tailing slope of the solvent peak. A calibration curve was determined over the analytical range 9.3-138 μg 2-nitropropane in 1.0 mL of ethyl acetate. This curve is shown in Figure 3.

### recoveries of analyte from Chromosorb 106

Samples for study of analyte recovery were prepared by applying measured amounts of 2-nitropropane in ethyl acetate to 100 mg beds of Chromosorb 106. Recoveries were determined over the range of 0.98-98 μg 2-nitropropane/sample. Twelve samples at each level were prepared; six were analyzed on the first day and the remainder 15 days after preparation. The results were compared to controls. The percent recoveries for the sample sets are shown in Table II.

### sampling

The analytical method was evaluated over the range 3.1-28.3 $mg/m^3$ 2-nitropropane in humid air by collecting 3.0 liter air samples at 0.05 L/min. Table III shows the recoveries at each level. The storageability of 2-nitropropane samples collected from humid environments on Chromosorb 106 was investigated at the lower useful end of the analytical range. Twenty-four 3-liter samples of an atmosphere containing 4.5 $mg/m^3$ (1.3 ppm) 2-nitropropane in humid air were obtained. The samples, collected six at a time, were grouped randomly into four sets of six each and analyzed at 1, 7, 14 and 28-day intervals after collection. All except day 1 samples were stored at room temperature for seven days; the two and four-week samples were refrigerated after the initial seven-day storage period at room temperature. The data obtained from the analyses of these samples are given in Table IV.

## results and discussion

The excellent agreement obtained between the analytical and independent methods is shown in Table III. The overall sampling and analytical precision was determined to be 0.05. This was determined according to methods outlined in Reference 4. The precision of the independent method was not determined.

It is interesting that Chromosorb 106, a cross-linked polystyrene porous polymer, had the highest capacity for 2-nitropropane. It was expected that the more polar sorbent Chromosorb 104, an acrylonitrile-divinylbenzene copolymer, would have a greater affinity for the analyte. The higher surface area of Chromosorb 106, relative to that of Chromosorb 104, may account for this result (see Table I). In addition, the water vapor present in the challenge atmosphere may compete with 2-nitropropane for polar sites on the Chromosorb 104 and reduce its collection efficiency. This effect also may account for the low capacity of silica gel. The retention volume also was affected by the mesh size of the Chromosorb 106, with the 60/80 mesh having a substantially greater capacity than the 20/40 mesh.

The calibration curve was based on collection of a 3.0 liter air sample; it is linear over the analytical range 9.3-138 μg/mL ethyl acetate. The equation of the linear least squares line (LLSQ) is $Y = 1.30 \times 10^4 Q - 5.45 \times 10^3$, where Q is the quantity of analyte collected in μg and Y is the integrated peak area response of the chromatograph. The linear correlation coefficient is 0.9995; the coefficient of variation (Sr) of the slope is 0.013.

Table II indicates that, at the 0.98 μg/sample level, the percent recoveries of 2-nitropropane from Chromosorb 106 ranged from 105% (Sr = 13.3) for the one-day storage to 83.4% (Sr = 32.1) for the 15-day storage. Although the recovery at this level was quantitative, it may be too imprecise. It is not clear whether the low values obtained after storage for 15 days were the result of irreversible adsorption or decomposition of the analyte on the sorbent. Due to the imprecision of the results at the 0.98 μg level, the lower useful limit of the analytical range has been established to be approximately 10 μg/sample (3.6 $mg/m^3$ for a 3-liter air sample). 2-Nitropropane samples collected from humid air at or above this minimum level are quantitatively recovered, even after storage for 28 days. Migration to the backup sections of the sorbent tubes did not occur during storage.

A sampling volume of three liters, collected at 0.05 L/min, was selected. Although the capacity of the sorbent is higher (5% breakthrough volume = 10.4 L at 200 $cm^3/min$), consideration must be given to the effect of the high pressure drop across the Chromosorb 106 bed on the capability of the sampling pump to maintain a constant flow during the collection period. Flow rate variations may have significant effects upon the analytical precision. For example, the relative standard deviation obtained from the analysis of six 3-liter samples collected with personal sampling pumps from an atmosphere containing 4.6 $mg/m^3$ 2-nitropropane in humid air was 16%. Flow rates varied from 106-168 $cm^3/min$. These were the *maximum* flow-rates obtainable

from the pumps with the sampling tubes in line. The pressure drops across the tubes ranged from 10-15 torr. When the flow-rates were adjusted to 50-60 $cm^3/min$, the pressure drops were reduced to 5-8 torr. The relative standard deviation of analysis of six 3-liter samples collected at these lower flow rates from an atmosphere containing 0.9 $mg/m^3$ 2-nitropropane in humid air was 6%. At the lower sampling rates, the pump flows were stable for at least one hour.


## acknowledgements

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