2-NITROPROPANE

Method no.:	15
Matrix:	Air
Target concentration:	25 ppm (90 mg/m^3) (OSHA PEL)
Procedure:	Collection on treated Chromosorb 106 tubes, desorption with ethyl acetate, analysis by GC using a flame ionization detector.
Detection limit based on recommended air volume: (for analytical procedure only)	0.27 ppm (0.98 mg/m^3)
Recommended air volume and sampling rate:	2 L at 0.2 L/min
Coefficient of variation:	0.023 (for analytical procedure only over the range of 0.54 ppm to 54 ppm based on the recommended air volume)
Special requirements:	Chromosorb 106 tubes are pretreated by placing them in a GC oven overnight at 120°C with a carrier gas flowing through them.
Status of method:	Evaluated method. This method has been subjected to the established evaluation procedures of the Organic Methods Evaluation Branch.

Date: January 1980 Chemist: Duane Lee

Organic Methods Evaluation Branch
OSHA Analytical Laboratory
Salt Lake City Utah

1. General Discussion

1.1. Background

1.1.1. History

A number of early analytical procedures for nitro paraffins are reported in the literature (Ref. 5.1.). The only procedure found which is directed towards industrial hygiene application is a colorimetric procedure in which the samples are collected in concentrated sulfuric acid (Ref. 5.2.). The 2-nitropropane is decomposed to nitrous acid which is combined with resorcinol to form a product which is suitable for quantitative measurement. Typically, this method suffers specificity problems with secondary nitro compounds, as well as certain other nitro compounds, which give positive responses.

The most common procedure for determining air concentrations of solvent vapors is collection of the vapors with charcoal adsorbent tubes and analysis by GC after desorption with carbon disulfide. When this procedure is used to determine 2-nitropropane there is a partial conversion of the analyte to acetone on the charcoal surface. This can be confirmed by the analysis of charcoal tubes spiked with 2-nitropropane. NIOSH produced a sampling and analytical method which calls for collection of air samples with Chromosorb 106 adsorbent tubes and analysis by GC after desorption with ethyl acetate (Ref. 5.3.). This procedure was selected for evaluation using OSHA evaluation procedures.

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

Exposure to concentrations of 2-nitropropane on the order of 20 to 45 ppm are reported to cause nausea, vomiting, diarrhea, loss of appetite, and severe headaches in humans (Ref. 5.4.). Concentrations of 165 to 445 ppm, cause nausea, dizziness, headaches, and diarrhea in humans (Ref. 5.5.). Cats, which died within 17 days of exposure to 328 ppm 2-nitropropane, sustained severe liver damage (Ref. 5.6.). Liver damage attributed to high concentrations of 2-nitropropane in humans has been reported (Ref. 5.7.). Liver cancer was found in rats exposed to 207 ppm 2-nitropropane for 6 months (Ref. 5.8.). These data raise the question of carcinogenic effects in humans. While additional studies are in progress, NIOSH believes it would be prudent to handle 2-nitropropane as if it were a human carcinogen (Ref. 5.8.).

1.1.3. Work population

An estimated 100,000 workers are potentially exposed to 2-nitropropane (Ref. 5.8.).

1.1.4. Use and operations where exposure occur

The following information is taken directly from Reference 5.8.

> Solvent systems containing 2-nitropropane are used in coatings (e.g., vinyl, epoxy, nitrocellulose, and chlorinated rubber), printing inks, and adhesives. Occupational exposure to these products may occur in various industries including industrial construction and maintenance, printing (rotogravure and flexographic inks), highway maintenance (traffic markings), shipbuilding and maintenance (marine coatings), furniture, food packaging, and plastic products.

1.1.5. Physical properties (Refs. 5.9. and 5.10.)

molecular weight:	89.09
density at 25°C:	0.98290 g/mL
melting point:	-91.32°C
boiling point:	120°C
vapor pressure at 20°C:	12.9 mmHg
vapor density (air =1):	3.06
flash point:	103°F
refractive index:	1.39439

critical temperature:	344°C
ignition temperature:	802°F
lower flammability limit (% by vol. in air):	2.6
solubility at 25°C,(% by wt compound in water):	1.7
wt water in compound:	0.5
molecular structure:	CH_3-CH-CH_3 | NO_2
other names:	dimethylnitromethane; isonitropropane; 2-NP; nitroisopropane

1.2. Detection limit, precision, sensitivity and working range

1.2.1. The detection limit for the analytical procedure is 2 ng per injection with a coefficient of variation of 0.055 at this level. (Section 4.1.) The detection limit was determined using 1.0-µL injections.

1.2.2. The pooled coefficient of variation of the analytical procedure over the range of 3.95 to 395 µg per sample is 0.023. (Section 4.2.) This represents an air concentration range of 0.54 to 54 ppm based on the recommended sampling and analytical procedures.

1.2.3. The sensitivity of the analytical procedure over a concentration range representing 0.02 to 2 times the target concentration based on the recommended air volume is 916.6 area units per µg/mL. The sensitivity is determined by the slope of the calibration curve (Section 4.2.) The sensitivity will vary somewhat with the particular instrumentation used in the analysis.

1.2.4. The lower limit of the estimated working range, assuming adequate desorption efficiency, is 0.27 ppm. The upper limit of the working range is dependent on the capacity of the collection medium.

1.3. Accuracy

1.3.1. The overall procedure must provide results that are within 25% or better at the 95% confidence interval.

1.3.2. The recovery of analyte from the collection medium after storage must be 75% or greater.

1.3.3. The overall procedure has met the above validation criteria. (Section 4.3.)

1.4. Advantages

1.4.1. The sampling procedure is convenient.

1.4.2. The analytical procedure is quick, sensitive, and reproducible.

1.5. Disadvantages

If other compounds are present, the GC run time must be lengthened so the late eluters will not interfere with the next sample.

2. Sampling Procedure

2.1. Apparatus

2.1.1. An approved and calibrated personal sampling pump whose flow can be determined within ±5% at the recommended flow.

2.1.2. Chromosorb 106 tubes: Glass tube with both ends heat sealed, 7 cm × 6-mm o.d. × 4-mm i.d., containing 100-mg front and 50-mg backup sections of Chromosorb 106 (60/80 mesh). SKC tubes or equivalent.

2.1.3. The Chromosorb 106 tubes are conditioned prior to use by heating overnight in a GC oven at 120°C with a carrier gas of helium or nitrogen flowing through the tubes. Conditioning removes residual components from the Chromosorb 106 which may interfere with the analysis.

2.2. Reagents

None required.

2.3. Sampling technique

2.3.1. Immediately before sampling, remove the caps of the Chromosorb 106 tube. All tubes must be from the same lot.

2.3.2. Connect the Chromosorb 106 tube to the sampling pump with flexible tubing. The short section of the Chromosorb 106 tube is used as a backup and should be positioned nearer the sampling pump.

2.3.3. The tube should be placed in a vertical position during sampling to minimize channeling.

2.3.4. Air being sampled should not pass through any hose or tubing before entering the Chromosorb 106 tube.

2.3.5. Seal the Chromosorb 106 tube with plastic caps immediately after sampling. Also, seal each sample with OSHA sealing tape lengthwise.

2.3.6. With each batch of samples, submit at least one blank tube from the same lot used for samples. This tube should be subjected to exactly the same handling as the samples (open, seal, transport) except that no air is drawn through it.

2.3.7. Transport the samples (and corresponding paperwork) to the lab for analysis.

2.3.8. If bulk samples are submitted for analysis, they should be transported in glass containers with Teflon-lined caps. These samples must not be put in the same container used for the Chromosorb 106 tubes.

2.4. Breakthrough

Breakthrough tests were performed with the primary section of Chromosorb 106 tubes using a controlled test atmosphere containing 52 ppm 2-nitropropane with an average relative humidity of 82% at 21°C. The 5% breakthrough volume was 5 L. Breakthrough was determined by monitoring the downstream effluent.

2.5. Desorption efficiency

The desorption efficiency from liquid injections on Chromosorb 106 tubes averaged 99.3% for 99 to 395 µg per tube, which is 13.6 to 54 ppm for a 2-L air volume. (Section 4.4.)

2.6. Recommended air volume and sampling rate

2.6.1. The recommended air volume is 2 L.

2.6.2. The recommended sampling rate is 0.2 L/min.

2.6.3. If a longer sampling time is required, a sampling rate of 0.05 L/min to 0.1 L/min can be used.

2.7. Interferences (sampling)

2.7.1. At the present time, it is unknown if any compound would severely interfere with the collection of 2-nitropropane on Chromosorb 106. In general, the presence of other solvents will decrease the breakthrough air volume for a particular solvent.

2.7.2. Any compound which is suspected of interfering in the collection or analysis

should be listed on the sampling data sheet.

2.8. Safety precautions

2.8.1. The broken ends of the tubes should be protected to avoid injury to the person being sampled.

2.8.2. When working in environments containing flammable vapors, do not provide any spark source from equipment used or pumps.

2.8.3. Observe all safety practices for working in hazardous areas.

3. Analytical Procedure

3.1. Apparatus

3.1.1. A GC equipped with a flame ionization detector.

3.1.2. A number of GC columns are available and adequate. The column used for this study was a 1/8-in. × 10-ft, stainless steel, 7% Tetracyanoethylated Pentaerythritol on 100/120 mesh Chromosorb P-AW.

3.1.3. An electronic integrator or other suitable method of measuring peak areas.

3.1.4. Two-milliliter vials with Teflon-lined caps.

3.1.5. Microliter syringes, 10-µL for preparing standards, 1-µL for sample injections.

3.1.6. Pipets for diluting standards. A 1.0-mL pipet for dispensing solvent for desorption, or a 1.0-mL repipet dispenser.

3.1.7. Volumetric flasks, convenient sizes for preparing standards.

3.2. Reagents

3.2.1. Ethyl acetate, chromatographic grade.

3.2.2. 2-Nitropropane, reagent grade.

3.2.3. Purified GC grade helium, hydrogen, and air.

3.3. Standard preparation

3.3.1. Standards are prepared by diluting pure 2-nitropropane with ethyl acetate.

3.3.2. Five microliters of 2-nitropropane per 25 mL of ethyl acetate is equivalent to 27.1 ppm for a 2-L air sample desorbed with 1.0 mL of ethyl acetate.

3.4. Sample preparation

3.4.1. The front and back sections of each sample are transferred to separate 2-mL vials.

3.4.2. Each section is desorbed with 1.0 mL of ethyl acetate.

3.4.3. The vials are sealed immediately and allowed to desorb for 30 min with intermittent shaking.

3.5. Analysis

3.5.1. GC conditions:

helium (carrier gas) flow rate:	25 mL/min
detector (flame ionization)	
hydrogen flow:	30 mL/min
air flow:	240 mL/min

injector temperature:	150°C
detector temperature:	250°C
column temperature:	100°C
injection size:	1.0 µL

3.5.2. Chromatogram

A typical chromatogram of 2-nitropropane, using the recommended GC conditions, is shown in Figure 3.5.2. The concentration was 197.5 µg/mL (27.1 ppm) and the injection size was 1 µL. The larger peak is ethyl acetate and the smaller peak (7.55 min) is 2-nitropropane.

3.5.3. Peak areas are measured by an electronic integrator or other suitable means.

3.5.4. An external standard procedure is used. The integrator is calibrated to report results in ppm for a 2-L air sample after correction for desorption efficiency.

3.6. Interferences (analytical)

3.6.1. Any compound having the same general retention time as 2-nitropropane is an interference. Possible interferences are listed on the sample data sheets. GC parameters should be chosen so these interferences will pose no problems.

3.6.2. GC parameters may be changed to circumvent most interferences.

3.6.3. Retention time on a single column is not considered proof of chemical identity. Samples should be confirmed by GC/MS or other suitable means.

3.7. Calculations

Usually the integrator is programmed to report for a 2-L air sample. The following calculation is used:

ppm = A/(B/2) where A = ppm on report
B = air volume (L)

3.8. Safety precautions

3.8.1. All work using solvents (preparation of standards, desorption of samples, etc.) should be done in a hood.

3.8.2. Avoid any skin contact with all of the solvents.

3.8.3. Safety glasses should be worn throughout the procedure.

4. Backup Data

4.1. Detection limit

A small amount of analyte (1.98 ng/injection) which produced a well defined peak was designated as the analytical detection limit. This was determined with an analytical standard which contained 0.002 µL of 2-nitropropane per milliliter of ethyl acetate (1.98 µg/mL).

Reproducibility of the peak produced by 1.98 ng was good. Eight injections resulted in a coefficient of variation of 5.5%.

A sample collected from 2 L of air which contained 1.98 ng/µL after desorption with 1 mL of ethyl acetate would represent an air concentration of 0.27 ppm.

4.2. Precision data

Multiple injections were made of the standards that were prepared over a range of 0.02 to 2.2 times the target concentration. A standard deviation and a coefficient of variation was determined at each concentration. The pooled coefficient of variation was determined for the range.

Table 4.2.
Analytical Precision

x target conc. µg/sample	0.02x 3.95	0.1x 19.57	0.54x 98.76	1.1x 197.52	2.2x 395.04
area counts	3785	19266	93540	183170	372497
	3620	19397	93869	185086	372586
	3814	19095	96997	182714	360046
	3672	19126	91388	186600	345140
$\bar{X}$	3723	19221	93948	184393	362567
SD	92	139	2311	1795	13026
CV	0.0247	0.0072	0.0246	0.0097	0.0359

$\overline{CV}$ = 0.023

4.3. Storage data

Samples were collected on Chromosorb 106 from a generated atmosphere containing 25.3 ppm 2-nitropropane with an average relative humidity of about 81% at 22°C. A storage study was then conducted in which the collected samples were divided into two groups; one stored at ambient temperature and the other under refrigeration. Every few days, three samples from each group were analyzed. The results are shown in Table 4.3. and in Figures 4.3.1. and 4.3.2.

Table 4.3.
Storage Tests

storage time (days)	% recovery (≈1°C to 6°C)			(21.3°C to 23°C)		
1	89.6	90.4	94.0	88.9	88.5	90.0
3	85.8	lost	87.2	86.9	91.9	96.5
6	96.2	95.0	96.8	84.4	91.8	89.4
10	112.4	112.9	112.3	103.4	92.4	89.7
12	99.7	100.0	104.9	90.0	92.6	97.8
14	101.4	94.7	100.6	90.6	77.2	78.8

4.4. Desorption efficiency

Liquid injections were made on the front section of conditioned Chromosorb 106 tubes at approximately 0.5, 1, and 2 times the target concentration. These were refrigerated overnight, desorbed and analyzed the following day. The overall desorption for the concentration studied is 99.3%.

Table 4.4.
Desorption Efficiency

× target concn µg/sample	0.5× 98.76	1× 197.5	2 × 395.0
desorption efficiency, %			
	111.7	98.4	97.0
	104.9	100.4	97.2
	92.8	99.2	95.7
	103.7	92.1	95.9
	106.6	95.1	99.0
ave	103.9	97.0	97.0

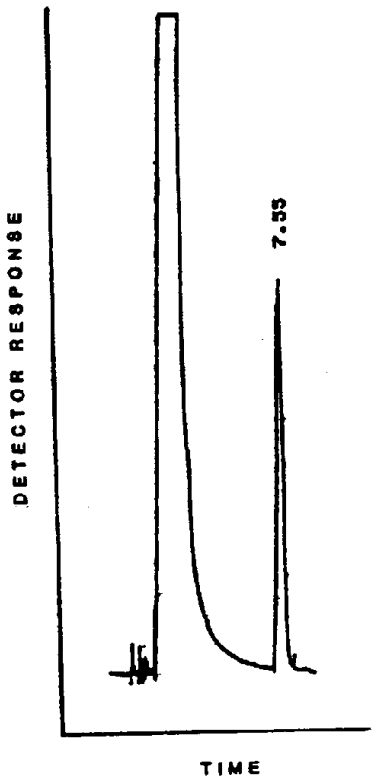

Figure 3.5.2. Chromatogram of a standard of 2-nitropropane.

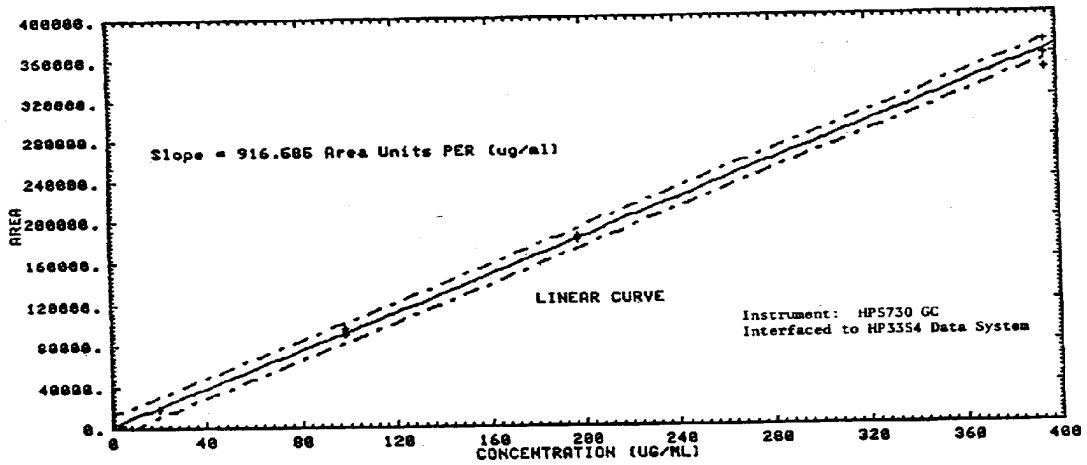

Figure 4.2. Calibration curve of instrument response to 2-nitropropane.

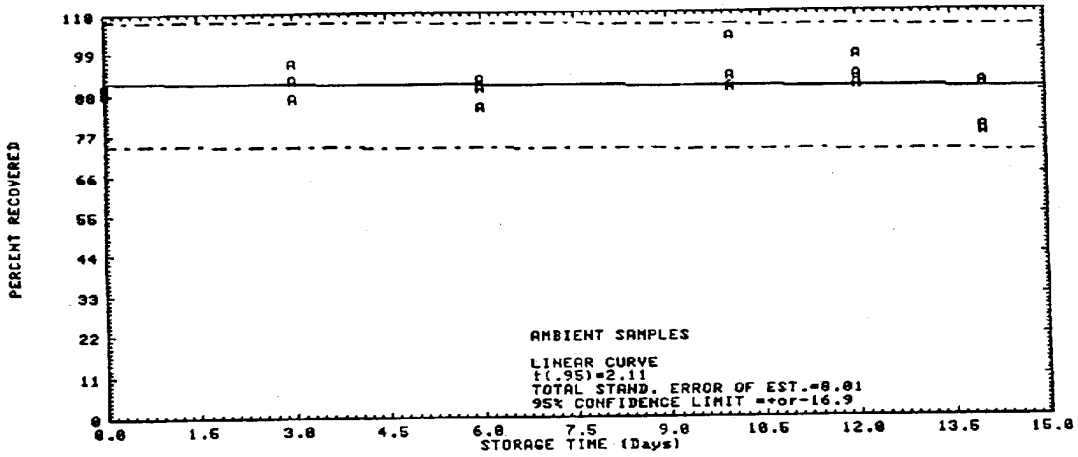

Figure 4.3.1. Ambient storage test of 2-nitropropane.

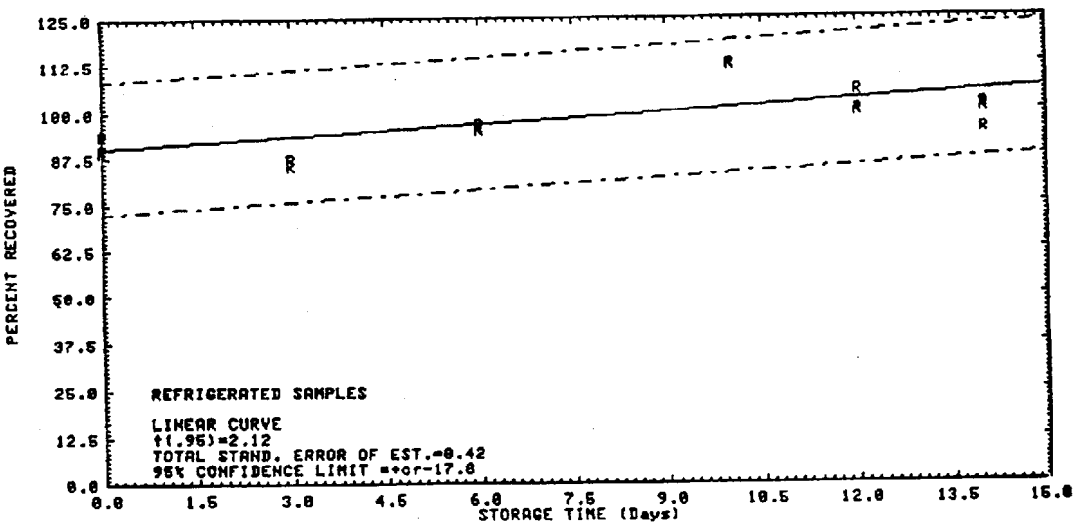

Figure 4.3.2. Refrigerated storage test of 2-nitropropane.

5. References

5.1. Standen, A. (Ed.), "Kirk-Othmer Encyclopedia of Chemical Technology". 2nd ed., New York: Interscience Publishers, Vol. 13, pp 875-876, 1964.

5.2. Jones, L. R., American Industrial Hygiene Association Journal, 24, 11-16, 1963.

5.3. Taylor, D. G. (Manual Coordinator) "NIOSH Manual of Analytical Methods". 2nd Edition, U.S. DHEW/PHS/CDC/NIOSH, Vol. 4, Method No. P&CAM 272, 1978.

5.4. Skinner, J. B., Ind. Med., 16, 441, 1974.

5.5. "Documentation of Threshold Limit Values", American Conference of Governmental Industrial Hygienists, 3rd Ed., p. 188-189, 1971.

5.6. Freon and Dutra Arch. Ind. Hyg. and Occ. Med., 5, 52, 1952.

5.7. Gaultier, M., et.al., Arch. I. Mal. Prof., 25, 425, 1964.

5.8. U.S. DHEW/PHS/CDC/NIOSH "Current Intelligence Bulletin 17" DHEW (NIOSH), April 25, 1977.

5.9. Patty, F. A. (Ed.) "Industrial Hygiene and Toxicology", 2nd ed., New York: John Wiley and Sons, Inc., p. 2073, 1963.

5.10. Standen, A. (Ed.), "Kirk-Othmer Encyclopedia of Chemical Technology". 2nd ed., New York: Interscience Publishers, Vol. 13, p. 866, 1964.