Analyte:	1-Chloro-1-nitropropane	Method No.:	S211
Matrix:	Air	Range:	51-206 mg/cu m
OSHA Standard:	20 ppm (100 mg/cu m)	Precision ($\overline{CV}_T$):	0.094
Procedure:	Adsorption on Chromosorb 108, desorption with ethyl acetate, GC/FID	Validation Date:	4/14/78

1. Synopsis

1.1 A known volume of air is drawn through a tube containing Chromosorb 108 to trap the organic vapors present. The sampling tube consists of a front adsorbing section and a backup section.

The Chromosorb 108 in each tube is transferred to respective vials and the 1-chloro-1-nitropropane is desorbed with ethyl acetate. An aliquot of this sample solution is injected into a gas chromatograph equipped with a flame ionization detector.

The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

2. Working Range, Sensitivity and Detection Limit

2.1 This method was validated over the range of 50.8-206.4 mg/cu m at atmospheric temperatures of 24.5 and 22.1°C, and atmospheric pressures of 765.4 and 767.9 mm Hg using a 12-liter sample volume. The method may be capable of measuring smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

The upper limit of the range of the method is dependent on the absorptive capacity of the Chromosorb 108. This capacity varies with the concentrations of 1-chloro-1-nitropropane and other substances in the air. When an atmosphere at 90% relative humidity containing 218.0 mg/cu m of 1-chloro-1-nitropropane was sampled at 0.2001 liter per minute, 5% breakthrough was observed after 111 minutes (capacity = 22.21 liters or 4.84 mg). The sample size recommended is less than two-thirds the 5% breakthrough capacity to minimize the probability of overloading the sampling tube.

The detection limit was not rigorously determined.

3. Interferences

3.1 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

3.2 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered as proof of chemical identity.

4. Precision and Accuracy

The Coefficient of Variation ($\overline{CV_T}$) for the total analytical and sampling method in the range of 50.8-206.4 mg/cu m was 0.0941. This value corresponds to a 9.41 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in References 11.1 and 11.2.

In validation experiments, this method was found to be capable of coming within ±25% of the "true value" on the average 95% of the time over the validation range. The concentrations measured at 0.5, 1, and 2 times the OSHA standard were 2.7% lower than the dynamically generated test concentrations (n = 18). The desorption efficiency was determined to be 0.912 for a collector loading of 0.605 mg. In storage stability studies, the mean of samples analyzed after seven days were within 1.7% of the mean of samples analyzed immediately after collection. Experiments performed in the validation study are described in Reference 11.2.

5. Advantages and Disadvantages

The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The collected samples are analyzed by means of a quick, instrumental method.

5.2 One disadvantage of the method is that the amount of sample that can be taken is limited by the number of milligrams that the tube will hold before overloading. When the amount of 1-chloro-1-nitropropane found on the backup Chromosorb 108 section exceeds 25% of that found on the front section, the probability of sample loss exists.

The precision of the method is affected by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and may cause the volume to be imprecise because the pump is usually calibrated for one tube only.

6. Apparatus

Sampling Equipment. The sampling unit for the sorbent collection method consists of the following components:

6.1.1 Sampling Pump. A calibrated personal sampling pump suitable for sampling at 0.2 liter per minute for 60 minutes. The pump must be accurate to within ±5% at the recommended flow rate.

6.1.2 Sampling Tubes. The sampling tube consists of a glass tube, flame-sealed at both ends, 10-cm long with a 10-mm O.D. and 8-mm I.D., packed with two sections of 60/80 mesh cleaned Chromosorb 108. The front adsorbing section contains 400 mg and the backup section contains 200 mg. The two sections are separated by a portion of silylated glass wool. A plug of silylated glass wool is placed at each end of the sorbent tube. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 0.2 liter per minute.

Gas chromatograph with a flame ionization detector.

Column, 20-ft x 1/8 in stainless steel, packed with 10% FFAP stationary phase on 100/120 mesh Supelcoport.

An electronic integrator or some other suitable method for measuring peak areas.

6.5 Microliter syringes, 10- and 100-microliter, and other convenient sizes for making standards and for taking sample aliquots.

Pipettes, 2-mL, delivery type.

Volumetric flasks, 10-mL or other convenient sizes for making standard solutions.

Sample vials, 5-mL with Teflon-lined screw caps.

7. Reagents

Wherever possible, reagents used should be ACS reagent grade or better.

1-Chloro-1-nitropropane, practical grade.

Ethyl acetate, reagent grade.

1-Heptanol, 99%, or other suitable internal standard. The appropriate solution of the internal standard is prepared in ethyl acetate.

Pre-cleaned Resin. Chromosorb 108 resin (60/80 mesh) is washed at least three times with methylene chloride in a separatory funnel using approximately 200 mL of solvent per 10 g of resin. The resin is washed next with ethyl acetate in a beaker of appropriate volume. The resin is then air-dried in a hood.

Nitrogen, purified.

Hydrogen, prepurified.

7.7 Air, filtered, compressed.

8. Procedure

Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent-washed and thoroughly rinsed with tap water and distilled water.

Calibration of Personal Sampling Pumps. Each personal sampling pump must be calibrated with a representative sorbent tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

Collection and Shipping of Samples

8.3.1 Immediately before sampling, the ends of the tubes should be broken so as to provide openings approximately one-half the internal diameter of the tubes (4-mm).

8.3.2 The section containing 200 mg of Chromosorb 108 is used as a backup and should be positioned nearest the sampling pump. The Chromosorb 108 tube should be maintained in a vertical position during sampling to avoid channeling and subsequent premature breakthrough of the analyte.

8.3.3 Air being sampled should not be passed through any hose or tubing before entering the front section of the Chromosorb 108 tube.

8.3.4 A sample size of 12 liters is recommended. Sample at a known flow rate between 0.2 and 0.04 liter per minute. Set the flow rate as accurately as possible using the manufacturer's directions. Record the necessary information to determine flow rate and also record the initial and final sampling time. Record the temperature and pressure of the atmosphere being sampled. If pressure reading is not available, record the elevation.

8.3.5 The Chromosorb 108 tubes should be labeled properly and capped with the supplied plastic caps immediately after sampling.

8.3.6 One Chromosorb 108 tube should be handled in the same manner as the sample tubes (break, seal, and transport), except for the taking of an air sample. This tube should be labeled as a blank. Submit one blank for every batch or partial batch of ten samples.

8.3.7 A sufficient number of unused Chromosorb 108 tubes should be available for use in desorption efficiency studies in conjunction with these samples, because desorption efficiency may vary from one batch of Chromosorb 108 to another. Record the batch number of the Chromosorb 108 used.

8.3.8 Capped Chromosorb 108 tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In preparation for analysis, each tube is scored with a file and broken open. The glass wool is removed and discarded. The Chromosorb 108 in each tube is transferred to a 5-mL screw-cap sample vial. Each tube is analyzed separately.

8.4.2 Desorption of Sample. Prior to analysis, 2.0 mL of ethyl acetate is pipetted into each sample vial. Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. The sample vials should be capped as soon as the solvent is added to minimize volatilization. For the internal standard method, desorb using 2.0 mL of ethyl acetate containing a known amount of internal standard.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 30 mL/min (60 psig) nitrogen carrier gas flow
2. 30 mL/min (25 psig) hydrogen gas flow to detector
3. 300 mL/min (60 psig) aid flow to detector
4. 225°C injector temperature
5. 250°C manifold temperature (detector)
6. 130°C column temperature

A retention time of approximately eleven minutes is to be expected for the analyte using these conditions and the column recommended in Section 6.3. The internal standard elutes in approximately eighteen minutes.

8.4.4 Injection of Sample. A 2-microliter aliquot of the sample solution is injected into the gas chromatograph. The

solvent flush method or other suitable alternative such as an automatic sample injector can be used provided that duplicate injections of a solution agree well. No more than a 3% difference in area is to be expected.

8.4.5 Measurement of Area. The signal of the sample peak is measured by an electronic integrator or some other suitable form of measurement such as peak height, and preliminary results are read from a standard curve prepared as discussed in Section 9.

8.5 Determination of Desorption Efficiency

8.5.1 Importance of Determination. The desorption efficiency of a particular compound may vary from one laboratory to another and also from one batch of Chromosorb 108 to another. Thus, it is necessary to determine the percentage of the specific compound that is removed in the desorption process for a particular batch of resin used for sample collection and over the concentration range of interest.

8.5.2 Preparation of Analytical Samples for Desorption Efficiency Determination. The desorption efficiency must be determined over the sample concentration range of interest. In order to determine the range which should be tested, the samples are analyzed first and then the analytical samples are prepared based on the amount of 1-chloro-1-nitropropane found in the samples.

The analytical samples are prepared as follows: Chromosorb 108, equivalent to the amount in the front section (400-mg), is measured into a 5-mL screw-cap vial. This resin must be from the same batch used in obtaining the samples. A known amount of a solution of 1-chloro-1-nitropropane in ethyl acetate (spiking solution) is injected directly into the resin by means of a microliter syringe. Adjust the concentration of the spiking solution such that no more than a 10-µL aliquot is used to prepare the analytical samples.

Six analytical samples at each of the three concentration levels (0.5, 1, and 2X the OSHA standard) are prepared by adding an amount of 1-chloro-1-nitropropane equivalent to a 12-liter sample at the selected level. A stock solution containing 241.8 milligrams of 1-chloro-1-nitropropane per milliliter of ethyl acetate is prepared. Aliquots (2.5, 5.0 and 10.0 µL) of the solution are added to the Chromosorb 108 vials to produce 0.5, 1 and 2X the OSHA standard level. The analytical samples are allowed to stand overnight to assure complete adsorption of the analyte onto the sorbent. A parallel blank vial is treated in the same manner except that no sample is added to it.

8.5.3 Desorption and Analysis. Desorption and analysis experiments are done on the analytical samples as described in Section 8.4. Calibration standards are prepared by adding the appropriate volume of spiking solution to 2.0 mL of ethyl acetate with the same syringe used in the preparation of the samples. Standards should be prepared and analyzed at the same time the sample analysis is done.

If the internal standard method is used, prepare calibration standards by using 2.0 mL of ethyl acetate containing a known amount of the internal standard.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the vial divided by the weight in mg added to the vial, or

$$D.E. = \frac{\text{Average Weight (mg) recovered - Resin Blank (mg)}}{\text{Weight (mg) added}}$$

The desorption efficiency may be dependent on the amount of 1-chloro-1-nitropropane collected on the sorbent. Plot the desorption efficiency versus weight of 1-chloro-1-nitropropane found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standardization

A series of standards varying in concentration over the range corresponding to 12-liter collections at 0.1-3 times the OSHA standard is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. This is done in order to minimize variations in FID response. It is convenient to express concentration of standards in terms of mg per 2.0 mL since the samples are desorbed in 2.0 mL of ethyl acetate. A calibration curve is established by plotting peak area versus concentration in mg per 2.0 mL.

Prepare a stock standard solution containing about 240 mg/mL of 1-chloro-1-nitropropane in ethyl acetate.

From the above stock solution, appropriate aliquots are added to 2.0 mL of ethyl acetate. Prepare at least five standards to cover the range of 0.12 - 3.6 milligrams/sample. The range is based on a 12-liter air sample.

For the internal standard method, use ethyl acetate containing a predetermined amount of the internal standard. The internal standard concentration used should be approximately 70% of the analyte concentration for a standard solution representing a 12-liter collection at 2X the OSHA standard. The area ratio of the analyte to that of the internal standard is plotted against the analyte concentration in mg per 2.0 mL.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed because the standard curve is based on mg per 2.0 mL and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the sample blank (Section 8.3) must be made for each sample:

$$mg = mg\ sample - mg\ blank$$

where:

mg sample = mg found in sample vial

mg blank = mg found in blank vial

A similar procedure is followed for the backup sections.

10.3 Add the weights found in the front and backup sections to determine the total weight of the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.3) for the amount found in the front section of the tube. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total Weight}}{\text{D.E.}}$$

10.5 Determine the volume of air sampled at ambient conditions in liters based on the appropriate information, such as flow rate in liters per minute multiplied by sampling time. If a pump using a rotameter for flow rate control was used for sample collection, a pressure and temperature correction must be made for the indicated flow rate. The expression for this correction is:

$$\text{Corrected Volume} = f \times t \left(\sqrt{\frac{P_1}{P_2} \times \frac{T_2}{T_1}} \right)$$

where:

f = sampling flow rate

t = sampling time

P_1 = pressure during calibration of sampling pump (mm Hg)

P_2 = pressure of air sampled (mm Hg)

T_1 = temperature during calibration of sampling pump (°K)

T_2 = temperature of air sampled (°K)

10.6 The concentration of the analyte in the air sampled can be expressed in mg per cu m which is numerically equal to µg per liter.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4) x 1000 (liter/cu m)}}{\text{Air Volume Sampled (liter)}}$$

Another method of expressing concentration is ppm (corrected to standard conditions of 25°C and 760 mm Hg).

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{123.54} \times \frac{760}{P} \times \frac{(T + 273)}{298}$$

where:

P = pressure (mm Hg) of air sampled
T = temperature (°C) of air sampled
24.45 = molar volume (liter/mole) at 25°C and 760 mm Hg
123.54 = molecular weight of 1-chloro-1-nitropropane
760 = standard pressure (mm Hg)
298 = standard temperature (°K)

11. References

Documentation of NIOSH Validation Tests, National Institute for Occupational Safety and Health, Cincinnati, Ohio (DHEW-NIOSH Publication No. 77-185), 1977. Available from Superintendent of Documents, U.S. Government Printing Office, Washington, D.C., Order No. 017-033-00231-2.

Backup Data Report for 1-Chloro-1-nitropropane, No. S211, prepared under NIOSH Contract No. 210-76-0123.