

State of California
Air Resources Board

Method 432

Determination of Dichloromethane and 1,1,1-Trichloroethane
in Paints and Coatings

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Method 432 - Determination of Dichloromethane and 1,1,1-Trichloroethane in Paints and Coatings

INTRODUCTION

This test method should only be attempted by persons familiar with operation of a gas chromatograph in a variety of analytical applications. This method is derived in large part from ASTM D4457-85, differing principally in requiring verification of instrument linearity and analysis of an audit specimen.

1 APPLICABILITY AND PRINCIPLE

1.1 Applicability

These procedures are applicable to measurement of the concentration, in weight percent, of dichloromethane and 1,1,1-trichloroethane in paint, coatings, and similar materials. They may be approved by the Executive Officer for measurement of other specific solvents in paints and coatings if it is demonstrated that accuracy in concentration can be obtained equivalent to that for dichloromethane and 1,1,1-trichloroethane.

1.2 Principle

The paint or coating material is mixed with a diluent compound and an internal standard in known gravimetric proportions, solids are removed by centrifuging if practical, and the weight concentration of specific compounds in the paint is found by gas chromatography. The suggested diluent is N, N-dimethylformamide and the suggested internal standard is 1-propanol; others may be used.

2 RANGE AND SENSITIVITY

The lower limit of sensitivity will vary according to the nature of the compound(s) of interest and the gas chromatography equipment used. The procedure is expected to be accurate in measuring concentration of specific volatile solvent compounds which constitute major constituents in paints and coatings. This method is not intended for measurement of trace level concentrations.

3 INTERFERENCES

Compounds with the same retention time as a compound of interest may interfere with measurement of that compound's peak. Parallel analysis with a referee column makes undetected interferences unlikely. Selection of a diluent or internal standard miscible with some coatings may, in rare instances, present difficulties.

4 APPARATUS

All apparatus surfaces which come in contact with sample materials should be of glass, stainless steel, or other substantially impermeable and unreactive material.

4.1 Gas Chromatograph System

Temperature programmable gas chromatograph with heated liquid injection port, thermal conductivity detector, and potentiometric strip chart recorder or equivalent (such as a data system).

4.1.1 Alternative Detectors. Other detector types may be used if compatible with expected concentrations and capable of properly measuring the compounds of interest.

4.2 Protective Pre-Column

A pre-column 4.0 inches (101 mm) long of 1/8 inch (3.2 millimeters) outside diameter stainless steel tubing and packed with glass wool, to be installed upstream of the analytical column to retain non-volatile materials and protect the analytical column, or similar provision, is recommended. It is advisable to also fit the injection port with a removable glass sleeve or liner arranged to retain most nonvolatile residues and facilitate cleanup.

4.3 Analytical Column

A main column 4 feet (1.22 m) long of 1/8 inch (3.2 millimeters) outside diameter stainless steel tubing, packed with 80/100 mesh (150-180 micrometer) porous polymer packing material such as "Porapak R", or other suitable column capable of adequately separating the compound(s) of interest from other constituents of the analyzed material.

4.4 Referee Column

A second column with characteristically different retention times shall be selected or assembled by the analyst for referee analyses to demonstrate freedom from interferences.

4.5 Paint Shaker

A mechanical paint shaker.

4.6 Centrifuge

Low speed centrifuge capable of operation at approximately 1000 revolutions per minute and equipped with a rotor compatible with the sample vials described below.

4.7 Balance

Automatic electronic balance, with draft shield, for rapid weighing of vials and contents to nearest milligram, used for weighing components added

to mixtures as described below.

4.8 Syringes

Microsyringes of 5 microliter or 1.0 microliter capacity, for transfer and injection of specimens for analysis.

4.9 Vials

Transparent glass vials, maximum 30 milliliter capacity, centrifugable and designed to be hermetically sealed with provision for repeated withdrawal of specimens with a microsyringe without substantial loss of contained vapors or exposure of contents to air.

4.9.1 Vial Sealing Supplies. Teflon-lined septum seals or special valves such as "Mininert" valves, together with appropriate installation or crimping materials and tools.

4.10 Regulators

Appropriate regulators for carrier gas in high pressure cylinders.

5 REAGENTS AND MATERIALS

5.1 Carrier Gas

Cylinders of hydrocarbon free or zero grade helium or 99.999% pure nitrogen as appropriate for operations with the detector and column selected.

5.2 Diluent

N, N-Dimethylformamide (DMF), 99+% pure, used for dilution of standards and coating materials. Another diluent compound should be substituted for N, N-Dimethylformamide if DMF is found to be immiscible with a particular coating material as described in procedures below or otherwise inappropriate.

5.3 Internal Standard

1-Propanol, 99+% pure, used as an internal standard as described below. Another appropriate compound of similar purity should be substituted for 1-propanol if the coating material to be analyzed contains 1-propanol or 1-propanol is otherwise inappropriate.

5.4 Pure Compound(s) of Interest

The specific organic compound of interest (such as 1,1,1-trichloroethane or dichloromethane), 99+% pure, used for preparation of standards as described below.

5.5 Audit Material

A uniform mixture containing the compounds of interest in known

gravimetric proportion, prepared from separate stocks of reagents similar to those above at a location and by persons outside the laboratory. This material is to be used only to check analytical performance and not for adjustment or calibration of the analytical system.

6 PREPARATION OF APPARATUS

6.1 Column Conditioning

New columns tend to "bleed" when heated to necessary operating temperatures, potentially contaminating the detector and deflecting the recorder baseline. New columns should be preconditioned as necessary to achieve a good recorder baseline. Consult the packing and instrument manufacturer's recommendations for specific procedures. A suggested procedure for "Poropak R" columns is described in the following steps:

6.1.1 Disconnect the column exit from the detector to avoid detector contamination.

6.1.2 Set carrier gas (helium) flow to 30 mL/min.

6.1.3 Purge unheated column 5 - 10 min.

6.1.4 Heat column 5 degrees C/min to 200 degrees C and purge approximately 12 hours.

6.1.5 Increase column temperature 5 degrees C/min to 240 degrees C (10 degrees C below maximum temperature allowable for packing) and continue purging for several hours (at least three).

6.1.6 Allow column to cool, reconnect column to detector, and increase column temperature 5 degrees C per minute to 240 degrees C to observe column bleed; discontinue heating if recorder baseline is not good.

6.1.7 If necessary repeat above steps until a good recorder baseline is achieved.

6.2 Establish Operating Routine

Establish in writing a well defined operating routine for the specific gas chromatograph system used. The procedure should be consistent with the instrument manufacturer's recommendations and with prior experience with the system. Once established, this operating routine should be adhered to uniformly to promote consistent system performance. The operating routine should describe the gas chromatograph system's component instruments and include specification of the operating parameters listed below where applicable and such other

conditions and settings as may be necessary for proper, uniform operation of the system.

6.2.1 Operating conditions to be specified.

6.2.1.1 Carrier gas type (helium or nitrogen) and flow rate.

6.2.1.2 System warm up schedule and procedure.

6.2.1.3 Injection port temperature.

6.2.1.4 Column temperature program including:

6.2.1.4.1 Pre-injection column temperature and stabilization time,

6.2.1.4.2 Post-injection column temperature increase rate or schedule, and

6.2.1.4.3 Final column temperature and minimum dwell time.

6.2.1.5 Detector/recorder configuration and settings, including chart speed.

6.2.1.6 Nominal injection size.

6.2.2 Recommended Operating Conditions for Preferred Column. A recommended operating routine for the suggested 1/8 inch by 4 foot "Porapak R" column is provided here.

6.2.2.1 Carrier gas

6.2.2.1.1 Type: Helium

6.2.2.1.2 Flow Rate: 30 milliliters per minute

6.2.2.2 System warm-up schedule: Condition column 1 hour at 200 degrees C with carrier gas flow each day prior to calibration and analysis. Reduce column temperature to 100 degrees C and allow system sufficient time to reach equilibrium as indicated by a stable recorder baseline.

6.2.2.3 Injection port temperature: 200 degrees C.

6.2.2.4 Column temperature program as follows:

6.2.2.4.1 Pre-injection column temperature: 100 degrees C for at least 3 minutes.

6.2.2.4.2 Post-injection column temperature increase rate 8 degrees C per minute.

6.2.2.4.3 Final column temperature 230 degrees C for at least 8 minutes.

6.2.2.5 A detector block temperature of 250 degrees C is recommended for thermal conductivity detectors if used. Detector/recorder configuration will vary with different instruments; other settings can not be specified here.

6.2.2.6 Nominal injection size 1 microliter.

6.3 Establish Appropriate Calibration Procedure

Establish a written calibration procedure appropriate to the specific gas chromatograph system. The procedure should be consistent with the instrument manufacturer's recommendations and with prior experience with the system. The procedure should provide for all physical and mathematical corrections of response necessary to make the corrected response directly proportional to the injected mass of each measured compound. Some systems may require daily preparation of a calibration curve to accomplish this while with other systems much simpler procedures may be adequate.

In general, daily calibration should include injection of at least one known mixture and appropriate verification or adjustment of recorder baseline position ("zeroing") and amplifier gain ("spanning"). Note that the analysis section below calls for injection of a response factor standard; this mixture may be used in the calibration procedure. The audit mixture described in the analysis section below may specifically not be used as a basis for calibration.

Commonly, uncorrected response to a compound is taken as the area under the peak produced by that compound, the time integral of recorder deflection from the "baseline". This is measured directly from the strip chart or with a data system. Application of mathematical corrections to peak area may be necessary. Some types of detectors produce a signal which is proportional not to concentration but to some function thereof such as the square root or logarithm. Some amplifiers are only approximately linear. Nonlinearity is common near the limit of any

detector's range.

6.4 Verify Gas Chromatograph Response Linearity

Verify the linearity of corrected gas chromatograph response by injecting a series of solutions of known concentration and density at least once every six months. A series of concentrations for each compound of interest is suggested; series for at least two different compounds are required.

Each series of solutions should include a blank and three mixtures containing approximately 2, 10 and 20 weight percent of the compound of interest (corresponds to 9, 46 and 92 weight percent in paint subsequently diluted to 5 parts in 23 by weight). Solutions should be prepared by methods similar to those described in the analysis section below, weighing each component as it is added to the mixture. To maintain precision the lowest concentration should be prepared by diluting the highest.

Solution density may be measured by injecting 1.00 milliliter (not microliter) of solution through a septum into a weighed sealed vial and reweighing.

Calculate the mass of the compound in an analytical injection of each solution.

Install the column and warm up and calibrate the gas chromatograph system according to established procedures. If a calibration curve is prepared it should not be based on the series of solutions used to verify linearity.

Inject a small specimen of known volume of a solution and record response; repeat at least twice. Repeat for other concentrations.

Plot average corrected response for each concentration against calculated mass injected. Draw a line from the point representing the largest response to the origin, or plot the linear regression line for mass as a function of response. Note the distance of each plotted point from the line, in a direction parallel to the mass axis. If the corrected response is found to be non-linear, improve the operating or calibration routines or repair or replace the instrument as necessary.

6.5 Determine Retention Times

Determine retention times for the internal standard and all compounds of interest by injecting small specimens of the pure compounds or known mixtures. Do not assume the order of elution when injecting mixtures. Verify that retention times are sufficiently repeatable that order of elution will not change from day to day.

6.6 Inspection of Equipment

Visually inspect all equipment for contamination or defects before and after use. Verify cleanliness of microsyringes by injection of blanks. Verify that calibration and maintenance of the electronic balance is current. Ensure that all material stocks are well labeled.

7 ANALYSIS PROCEDURE

7.1 Mix Paint

Shake the coating and audit materials on a mechanical shaker or mix thoroughly by other means, avoiding loss of volatiles.

7.2 Prepare Mixtures

In a hood prepare mixtures in known gravimetric proportions by weighing an empty vial and reweighing after adding each mixture component. Each addition should be at least one g. All weighings should be to the nearest milligram. Four different mixtures are required; their components and nominal proportions are specified below. The proportions recommended are values expected to produce uniform solutions of 1-propanol and most coating liquids in the recommended diluent, DMF. Mixture components should be added in the order given below to reduce evaporative loss of non-diluent volatiles; the diluent will generally immerse and reduce the vapor pressure of other ingredients and diluent evaporation is less critical. It is recommended that vials be loosely covered between additions of liquid. Seal each vial with a crimp-on septum seal or equivalent after weighing all additions to that vial. Label each sealed vial and shake by hand to mix contents.

7.2.1 Mixture 1 - Coating Analysis Mixture. Diluent 16 grams, internal standard 2 grams, coating material 5 grams. Sample from the middle of the coating container below the liquid surface. This mixture is to be used as described below to determine concentration of the compounds of interest in the coating material.

7.2.2 Mixture 2 - Coating Assay Mixture. Diluent 16 grams, coating material 5 grams. Sample from the middle of the coating container below the liquid surface. This mixture is to be used as described below to verify that the coating material does not contain the internal standard selected.

7.2.3 Mixture 3 - Audit Mixture. Diluent 16 grams, audit material 5 grams, internal standard 2 grams. This mixture is to be analyzed exactly as the paint mixture, to verify analytical capability, and is not to be used for calibration.

- 7.2.4 Mixture 4 - Response Factor Standard. Diluent 16 grams, internal standard 2 grams, compounds of interest 2 grams each. This mixture is to be used as described below to determine relative response factors. It is also used to verify retention times.
- 7.3 Centrifuge Paint Mixtures
Centrifuge the mixtures containing the coating material (mixture 1, the coating analysis mixture, and mixture 2, the coating assay mixture) to promote settling of solids. 1000 rpm for five minutes is appropriate with some centrifuges; excessive centrifugal force can fracture some containers or dislodge septa. Only the supernatant should be injected in steps below. In situations where centrifuging is impractical or ineffective it may be omitted.
- 7.4 Examine Mixtures
Examine all vials visually. If two liquid phases are apparent, stop work and seek an alternative diluent miscible with both the coating liquid and the internal standard.
- 7.5 Analyze Specimens of All Mixtures
Install the column. Warm up and calibrate the gas chromatograph system according to established procedures. Each day inject a small specimen of each of the four mixtures and record response for each injection. Inject only the supernatant liquid when analyzing centrifuged coating mixtures. Inject each mixture at least twice unless no difference between repeat injections is probable. Audit and response factor injections need not be performed for each coating analyzed but must be performed twice daily.
- 7.6 Verify Retention Times
Examine the chromatograms from injections of mixture 4, the response factor standard, to verify that retention times are as expected.
- 7.7 Check for Internal Standard in Paint
Verify that the coating material does not contain the internal standard by examining the chromatograms from injections of mixture 2, the coating assay mixture. If the coating contains the internal standard stop work and use another compound as the internal standard.
- 7.8 Examine Peaks for Interferences
Examine the shape of pertinent peaks (internal standard, compounds of interest) on the paint's chromatogram and compare to the shape of peaks on the chromatogram resulting from injection of mixture 4 (the standard used for determining response ratios). Distortion of peak shape can show that the peak has been overlapped by a peak produced by an interfering compound. The absence of apparent distortion does not however guarantee that an interferent is not present.

7.9 Referee Analysis

Repeat the analysis with the referee column unless the formulation of the coating material is well known, retention times are known for all components, and no interferences are anticipated. If an interferent is present in analysis with either column the concentration measured with that column will be higher; consider the lower result correct.

8 CALCULATIONS AND NOMENCLATURE

8.1 Nomenclature

munk	=	weight of compound of interest added to standard mixture, grams
mis	=	weight of internal standard added to standard mixture, grams
runk	=	corrected response to compound of interest in one injection of standard mixture
ris	=	corrected response to internal standard in the same injection of standard mixture
R	=	ratio of response factors
C	=	concentration of compound of interest in coating material, weight percent
mp	=	weight of coating material added to paint mixture, grams
misp	=	weight of internal standard added to paint mixture, grams
runkp	=	average corrected response to compound of interest in injections of paint mixture
risp	=	average corrected response to internal standard in injections of paint mixture
V	=	volume of compound of interest in 1 liter of paint or audit material, liter/liter
G	=	grams of compound of interest in a liter of paint or audit material, grams/liter

D	=	density of the paint or audit material measured using ASTM Method D1475 or by other appropriate means, grams/liter
d	=	density of compound of interest, grams/liter of the compound as liquid at 68 degrees F in equilibrium with it's vapor
WtVOCinLiter	=	weight of volatile organic compounds in a liter of paint as applied, grams per liter without volume exclusions
VOCperLiter	=	corrected weight of volatile organic compounds in a liter of paint, grams per liter excluding exempt volatile components such as water
TotalExemptVolume	=	total volume of all exempt volatile components such as water in a liter of paint as applied, the volume V of each such component to be calculated from it's weight fraction or percent and it's density. Units of the total are liters/liter.

8.2 Calculations

For each compound of interest calculate the response factor ratio and the weight percent using values of munk, runk, and runkp for that particular compound. Applicability of other calculations depends on local regulations.

8.2.1 Response Factor Ratio Calculation

$$R = \frac{\left(\frac{\text{munk}}{\text{mis}} \right)}{\left(\frac{\text{runk}}{\text{ris}} \right)}$$

8.2.2 Weight Percent Calculation

$$C = \frac{(100\%) (\text{misp}) R \left(\frac{\text{runkp}}{\text{risp}} \right)}{(\text{mp})}$$

8.2.3 Volume-per-liter Calculation

$$V = \frac{C \left(\frac{D}{d} \right)}{100\%}$$

8.2.4 Grams-per-liter Calculation

$$G = \frac{CD}{100\%}$$

9 APPLICATION TO COATINGS RULES

Some Air Pollution Control District/Air Quality Management District coatings rules specify limitations on volatile organic compounds (VOC) in terms of "grams VOC per liter less water". Some rules exempt certain specific volatile organic compounds, such as 1,1,1-trichloroethane and dichloromethane, from consideration as VOC. The following correction for water and any specific exempted volatile organic compounds shall be made unless contradicted by calculations specified in applicable district rules:

$$\text{VOCperLiter} = \frac{\text{WtVOCinLiter}}{(1 - V_{EV})}$$

Where:

VOCperLiter is the quantity to be compared to the applicable VOC content limit;

WtVOCinLiter is the uncorrected quantity for the coating as determined using appropriate methods such as "ASTM D2369-81 Standard Test Method for Volatile Content of Coatings" supplemented by analysis for each exempt volatile compound;

V_{EV} is the total volume fraction of exempt volatiles, calculated as

$$V_{EV} = (V_{\text{water}} + V_1 + \dots + V_n)$$

where:

V_{water} is the volume fraction of water found in the coating using section 8.2.3 and an appropriate analysis method such as "ASTM D3792 - Standard Test Method for Water Content of Water Reducible Paints by Direct Injection into a Gas Chromatograph" or

"ASTM D4017 - Standard Test Method for Water in Paints and Paint Materials by Karl Fischer Method";

$V_1 . . . V_n$ are the volume fractions of any specific, exempted volatile organic compounds in the coating.

10 ALTERNATIVE TEST METHODS

The Executive Officer may approve an alternative test method, provided the executive officer finds the alternative method to be equivalent to this method. To make this finding the executive officer may require the person requesting the approval of the alternative test method to submit information needed to support the finding.