

SOUTH COAST AIR QUALITY MANAGEMENT DISTRICT

Technology Assessment to Determine the Relationship of Solvent Vapor Pressure and VOC Mass Emissions

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INTRODUCTION

In recent years, there has been much discussion on the role of solvent vapor pressure and its relation to reducing VOC emissions. Controlling VOC emissions by vapor pressure was first introduced in SCAQMD Rule 1124 (Aerospace Assembly and Component Manufacturing) in the late 1980s. The rule allowed cleanup solvents to have either a material VOC content of no more than 200 grams per liter or a VOC composite partial pressure of 45mm Hg at 68°F. It was believed that the option of allowing the use of a low vapor pressure solvent in lieu of a low VOC material would result in less VOC mass emissions than solvents with a higher VOC composite partial pressure.

Vapor pressure limits have since been incorporated into other solvent-related rules. In 1991, Rule 1171 (Solvent Cleaning Operations) was adopted with requirements limiting the VOC content and VOC composite partial pressure of cleanup solvents. However in October 1999, vapor pressure limits were eliminated from Rule 1171. At that time, staff determined that emissions from parts cleaned in batch cleaners and remote reservoirs were primarily caused by "drag-out" solvent and were independent of the vapor pressure of the solvent. Several industry representatives disagreed and claimed that lower vapor pressure solvents could result in viable mass emission reductions. The claims revolved around the use of low vapor pressure solvents for solvent hand-wiping activities. A Technology Assessment to study the relationship between vapor pressure and VOC mass emissions was identified as part of the Rule 1171 amendment.

PURPOSE

The purpose of this technology assessment is to determine whether the vapor pressure (termed VOC composite partial pressure in Rule 1171) of solvent cleaning materials affects VOC mass emissions to the atmosphere from solvent cleanup operations. Only emissions from wiped surfaces are considered in this evaluation.

TEST METHODS

Samples tested are typical non-aqueous hand-wipe solvents. Samples were included in the study that met previous Rule 1171 limitations but represented a range of vapor pressures. Prior to December 1, 2001, Rule 1171 vapor pressure limits ranged from 3mm Hg to 35mm Hg. Trends relating vapor pressure to VOC evaporation rates and emissions (if any) were determined. A few of the submitted samples contained exempt solvents.

Vapor pressure was measured using a modified ASTM D 323-99a Standard Test Method for Vapor Pressure of Petroleum Products (Reid Method) (see Attachment A). The method was modified by using a dry apparatus and maintaining the samples, cylinder, air chamber, and cup at ambient temperature for sample introduction. Vapor pressure readings were taken at 100°F. No attempt was made to estimate true vapor pressure since nomographs were not available for these samples. Readings were used to rank products and to determine trends.

Non-volatiles were measured using ASTM D 2369-01 Standard Test Method for Volatile Content of Coatings (see Attachment B). This method evaporates weighed aliquots at

110°C for one hour. Remaining material was weighed and calculated as "percent non-volatile". Density was measured using ASTM D 1475-98 Standard Test Method for Density of Liquid Coatings, Inks, and Related Products (see Attachment C). Water and exempt solvents were assumed to be zero. VOC mass was calculated in grams per liter of material.

Evaporation times (under field conditions) were estimated using a Dupont 951 Thermogravimetric Analyzer (TGA). TGA is an instrument that continuously measures weight loss over time under pre-determined airflow and temperatures. The TGA procedure approximates field conditions by using thin solvent films, low air velocities, non-absorbent substrates, and ambient temperatures. The instrument was programmed to run isothermally at ambient temperature with a dry air purge of approximately 100 sccm. This created a linear air velocity of about 0.4 cm/sec. Twenty to 30 microliters of sample were deposited on an empty, tared, 50 microliter platinum weighing pan. The resulting film thickness was approximately 0.2-0.4 mm. The overall evaporation rate of a sample was calculated as the ratio of the percent weight change over the time to dryness or constant weight.

Solvent cleaners were evaluated for vapor pressure, evaporation rate, and VOC content. Five (5) pure solvents were analyzed for reference purposes. Solvent cleaner vapor pressures were plotted against VOC content to determine if a positive correlation exists.

RESULTS

Samples

Eleven (11) samples of press cleaning materials were collected from local distributors for evaluation of vapor pressure, evaporation rate, and VOC content. The solvents were received in their typical commercial containers, along with their Material Safety Data Sheets (MSDS). Technical data obtained from each MSDS indicated that four (4) of the eleven (11) samples contained exempt solvents (acetone). These sample products are Prisco MRC-F, Prisco Autowash LA-3, Star Products #1001 Custom, and Star Products LVP-25 Custom. These products were included in the analysis to determine if meaningful data could be extracted from the results. Table 1 summarizes the solvent samples and technical data obtained from the MSDS for each of the solvent sample.

Table 1 - Properties of Solvent Samples (MSDS)

Sample Name	Specific Gravity	Vapor ⁽¹⁾ Pressure (mm Hg)	VOC (g/l)	Evaporation Rate ⁽²⁾	% Acetone	% Water
Prisco MRC-F	0.820	9.31	424	3.60	40-50	NL
Prisco Autowash LA-3	0.820	2.85	561	3.17	30-40	NL
Prisco UV#8	0.900	1.65	889	0.24	NL	NL
Prisco Superkleene 1IC	0.850	2.55	604	0.09	NL	NL
Prisco Superkleene 2P	0.830	2.70	821	0.29	NL	NL
Prisco Powerkleene VC	0.820	2.52	802	0.29	NL	NL
Prisco Autowash 6000	0.780	2.70	777	0.12	NL	NL
Star Product #250	0.790	21.87	790	>1	NL	NL
Star Product Ultra 2B	0.787	2.70	787	<1	NL	NL
Star Product #1001	0.762	28.77	683	>1	10	NL
Star Product LVP-25	0.781	5.00	587	<1	Listed ⁽³⁾	NL

Notes:

- (1) – Acetone partial pressure has been subtracted by the manufacturer.*
- (2) – Evaporation rates are reported relative to butyl acetate*
- (3) – Percent acetone was not listed on the MSDS.*

One of the samples, Prisco Superkleene 1IC, was observed to have a high non-volatile content and appearance that suggested the presence of water. Using ASTM D 4017-96a Standard Test Method for Water in Paints and Paint Material by Karl Fischer Method (see Attachment D) and ASTM D 2369-01 for non-volatiles, this sample was found to contain 14.3% water and 12.5% non-volatile residues. This sample did not meet the study profile and was excluded from discussion.

Vapor Pressure and Evaporation Rate

Vapor pressure measurements for ten remaining samples ranged from 0.62 psi (32 mm Hg) to 5.50 psi (284 mm Hg) at 100°F. Excluding the four (4) samples containing acetone, the vapor pressures ranged from 0.62 psi (32 mm Hg) to 2.26 psi (117 mm Hg). Only one (1) sample, Star Products #250 Wash, had a vapor pressure greater than 1 psi. The vapor pressures of the remaining samples were clustered between 0.62 psi (32 mm Hg) and 0.89 psi (46 mm Hg).

See Table 2 below for a summary of measured properties. A complete list of measured properties is found in Attachment E.

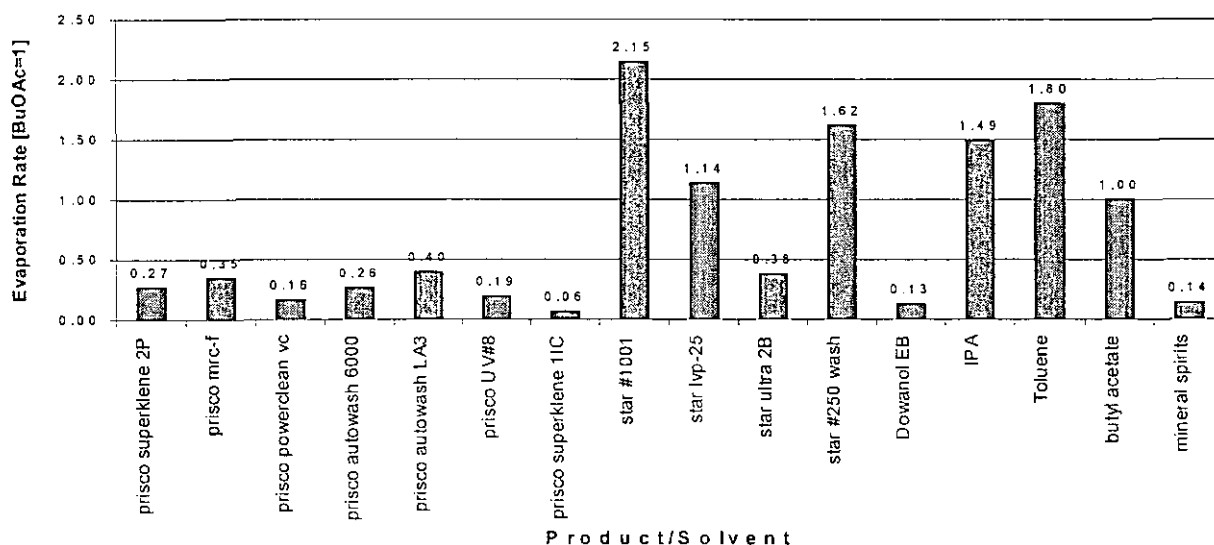
Table 2 – Measured Properties of Solvent Samples: Uncorrected for Acetone

Sample Name	Specific Gravity	VP (mm Hg)	VOC (g/l)	Evaporation Rate	T to constant wt (min)
Prisco MRC-F*	0.822	284	820	0.35	33
Prisco Autowash LA-3*	0.821	279	800	0.40	29
Star Product LVP-25*	0.781	279	780	1.14	10
Star Product #1001*	0.752	252	750	2.15	5
Star Product #250	0.788	117	790	1.62	7
Prisco Autowash 6000	0.790	46	780	0.26	43
Prisco Superkleene 2P	0.814	45	810	0.27	42
Star Product Ultra 2B	0.783	45	780	0.38	30
Prisco Powerkleene VC	0.829	40	810	0.16	70
Prisco UV#8	0.882	32	880	0.19	59
2-Propanol	0.782	116	780	1.49	8
Toluene	0.864	92	860	1.80	6
n-Butyl acetate	NA	NA	NA	1.00	11
Mineral spirits	NA	NA	NA	0.14	80
2-Butoxyethanol	0.900	23	900	0.13	89

* Samples containing acetone

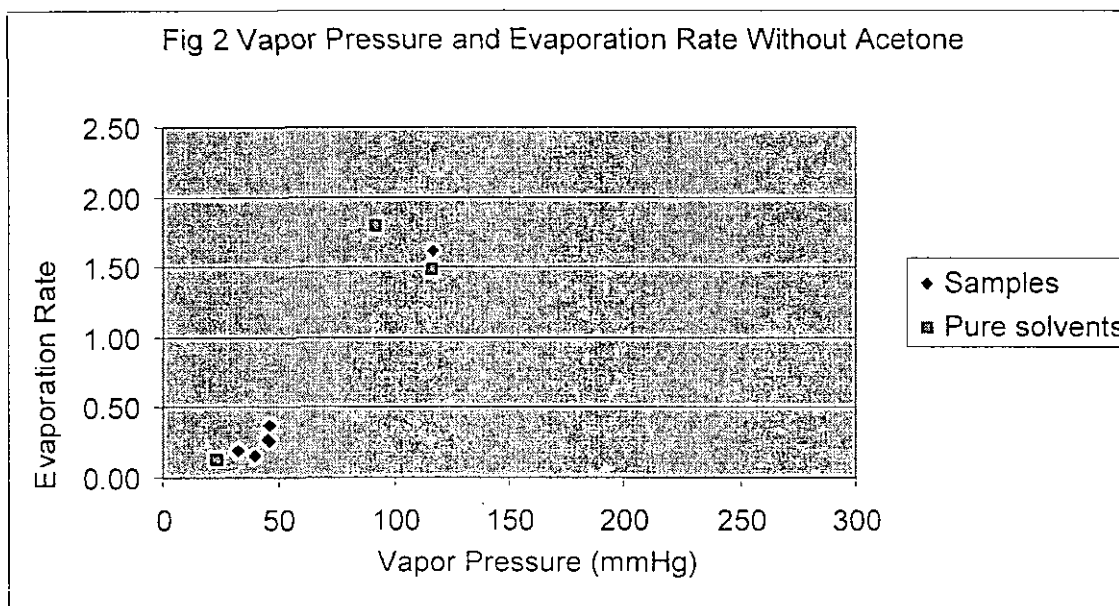
Table 2 shows that all samples demonstrated significant evaporation rates under conditions that approximate field conditions. Evaporation rates for all samples ranged from 0.16 to 2.15 (n-butyl acetate = 1). Evaporation rates were not invariably affected by the presence of acetone. Three (3) of four (4) samples containing acetone had evaporation rates (0.35 for Prisco MRC-F; 0.40 for Prisco Autowash LA-3; 1.14 for Star Products LVP-25) within the range of samples without acetone (0.16 to 1.62). A comparison of evaporation rates is shown in Figure 1. Evaporation rates for pure solvents have been included for reference purposes.

Figure 1 Evaporation Rates Relative to Butyl Acetate

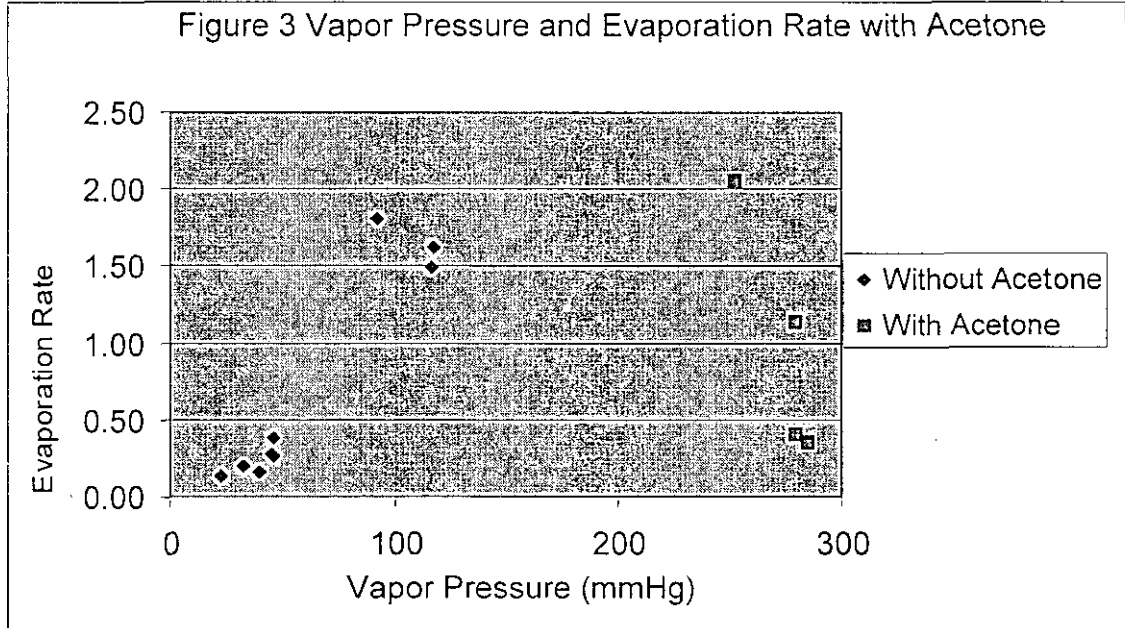


All ten samples evaporated within 70 minutes, and half of them evaporated within 30 minutes. Like evaporation rate, evaporation time was not necessarily tied to the presence of acetone. The overall evaporation time was ultimately determined by the evaporation rate of the *least* volatile component in the sample. This is demonstrated by the recorded evaporation curves. Solvents without acetone generated weight-loss curves similar in shape to those of pure solvents, but acetone-containing solvents yielded curves that demonstrated the evaporation of individual components, with acetone evaporating first and less volatile component(s) persisting. See Attachment F for recorded evaporation curves.

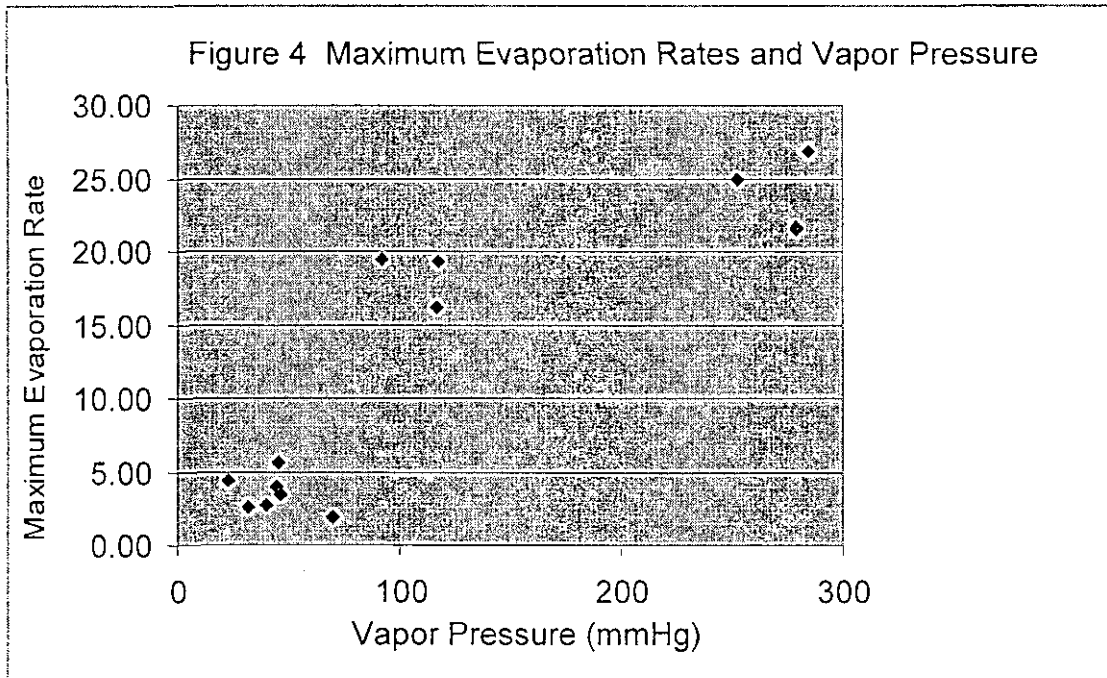
Excluding samples containing acetone, there is a positive correlation between vapor pressure and evaporation rate. The pure reference solvents analyzed in this study followed the same curve. (See Figure 2 below).



The inclusion of acetone-containing samples has a negative effect on correlation between vapor pressure and evaporation rate. See Figure 3 below.



Because acetone evaporates quickly, it affects maximum evaporation rate rather than the overall evaporation rate. When vapor pressure is plotted against the instantaneous maximum evaporation rate, the apparent outliers are restrained (see Figure 4).

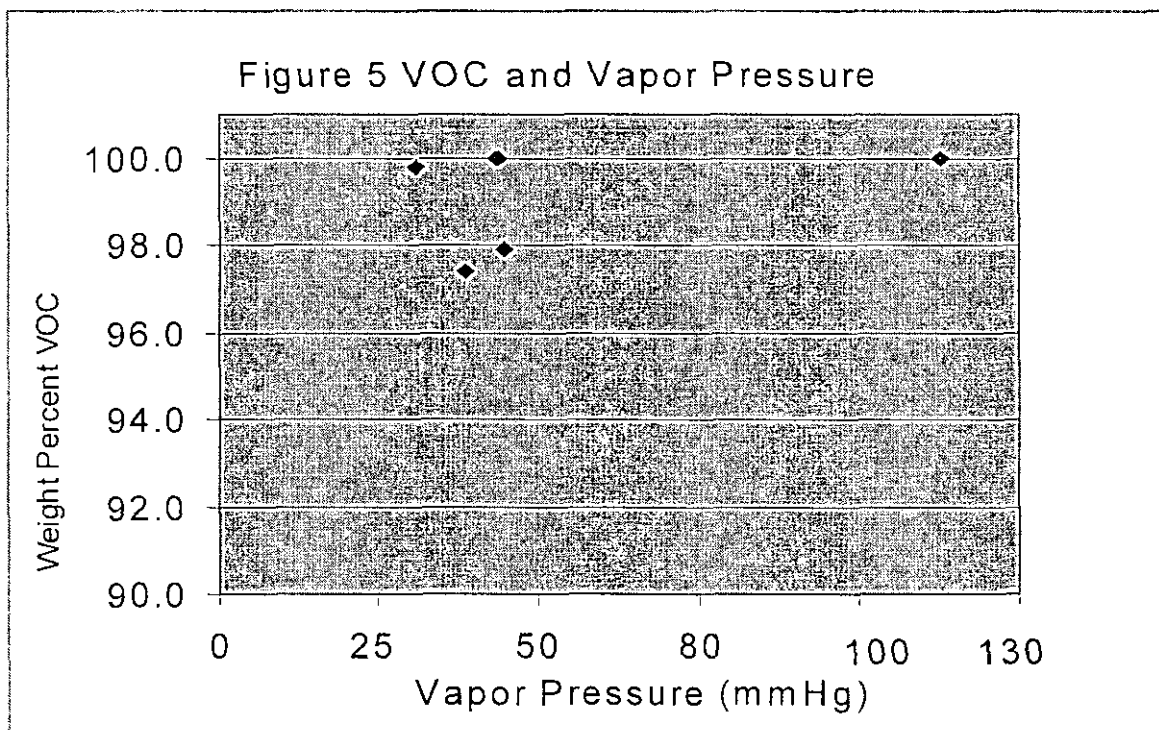


An attempt was made to subtract acetone vapor pressure from the measured vapor pressures of acetone-containing samples using the vapor pressure of acetone at 100°F and the amounts of acetone listed in the MSDS. However, since measured vapor pressures and acetone corrections were higher than the expected VOC vapor pressures by an order of

magnitude or more, the procedure didn't meet minimum requirements for data correction and the results were not reported.

Vapor Pressure and VOC

VOC values ranged from 750 to 880 grams per liter of material (excluding one sample that contained 14.3% water and 12.5% non-volatiles) as shown in Table 2. However, the differences in VOC values were caused primarily by differences in sample density and not in the percentage of volatile material. Recalculating the result as weight percent VOC provides a more realistic basis of comparison. Excluding samples containing acetone and water, the VOC content of the products ranged from 97.4% to 100%. There was no relationship between VOC content and vapor pressures in the range of samples that were evaluated (See Figure 5).



CONCLUSIONS

Based on the assessment, staff concludes that vapor pressure has no effect on VOC mass emissions. Even samples with very low vapor pressure tested at nearly 100% VOC. Vapor pressure does not appear to influence VOC mass emissions within the range of products and conditions that were studied; therefore, it is concluded that lower vapor pressure limits will not result in further reduction of VOC emissions.

Attachments

- A - ASTM D 323-99a Standard Test Method for Vapor Pressure of Petroleum Products
- B - ASTM D 2369-01 Standard Test Method for Volatile Content of Coatings
- C - ASTM D 1475-98 Standard Test Method for Density of Liquid Coatings, Inks and Related Products
- D - ASTM D 4017- 96a Standard Test Methods for Water in Paints and Paint Material by Karl Fischer Method
- E- Measured Parameters of Solvent Samples
- F- Recorded Evaporation Curves

**Technology Assessment to Determine the Relationship of Solvent Vapor
Pressure and Mass VOC Emissions**

Attachment A

ASTM D 323-99a

**Standard Test Method for Vapor Pressure
of Petroleum Products (Reid Method)**



Standard Test Method for Vapor Pressure of Petroleum Products (Reid Method)¹

This standard is issued under the fixed designation D 323; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

This standard has been approved for use by agencies of the Department of Defense.

1. Scope

1.1 This test method covers procedures for the determination of vapor pressure (see Note 1) of gasoline, volatile crude oil, and other volatile petroleum products. Procedure A is applicable to gasoline and other petroleum products with a vapor pressure of less than 180 kPa (26 psi). Procedure B may also be applicable to these other materials, but only gasoline was included in the interlaboratory test program to determine the precision of this test method. Neither procedure is applicable to liquefied petroleum gases or fuels containing oxygenated compounds other than methyl *t*-butyl ether (MTBE) (see Note 2). Procedure C is for materials with a vapor pressure of greater than 180 kPa (26 psi) and Procedure D for aviation gasoline with a vapor pressure of approximately 50 kPa (7 psi).

NOTE 1—Because the external atmospheric pressure is counteracted by the atmospheric pressure initially present in the vapor chamber, the Reid vapor pressure is an absolute pressure at 37.8°C (100°F) in kilopascals (pounds-force per square inch). The Reid vapor pressure differs from the true vapor pressure of the sample due to some small sample vaporization and the presence of water vapor and air in the confined space.

NOTE 2—For determination of the vapor pressure of liquefied petroleum gases refer to Test Method D 1267. For determination of the vapor pressure of gasoline-oxygenate blends refer to Test Method D 4953.

1.2 The values stated in SI units are to be regarded as the standard. The inch-pound units given in parentheses are provided for information only.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* Specific precautionary statements are given in Sections 6 and 17, and Note 6, Note 9, Note 12, Note 13, Note A1.1 and Note A1.2.

2. Referenced Documents

2.1 ASTM Standards:

D 1267 Test Method for Vapor Pressure of Liquefied Petroleum (LP) Gases (LP-Gas Method)²

D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products³

D 4953 Test Method for Vapor Pressure of Gasoline and Gasoline-Oxygenate Blends (Dry Method)⁴

E 1 Specification for ASTM Thermometers⁵

3. Summary of Test Method

3.1 The liquid chamber of the vapor pressure apparatus is filled with the chilled sample and connected to the vapor chamber that has been heated to 37.8°C (100°F) in a bath. The assembled apparatus is immersed in a bath at 37.8°C (100°F) until a constant pressure is observed. The reading, suitably corrected, is reported as the Reid vapor pressure.

3.2 All four procedures utilize liquid and vapor chambers of the same internal volume. Procedure B utilizes a semi-automatic apparatus immersed in a horizontal bath and rotated while attaining equilibrium. Either a Bourdon gage or pressure transducer may be used with this procedure. Procedure C utilizes a liquid chamber with two valved openings. Procedure D requires more stringent limits on the ratio of the liquid and vapor chambers.

4. Significance and Use

4.1 Vapor pressure is an important physical property of volatile liquids. This test method is used to determine the vapor pressure at 37.8°C (100°F) of petroleum products and crude oils with initial boiling point above 0°C (32°F).

4.2 Vapor pressure is critically important for both automotive and aviation gasolines, affecting starting, warmup, and tendency to vapor lock with high operating temperatures or high altitudes. Maximum vapor pressure limits for gasoline are legally mandated in some areas as a measure of air pollution control.

4.3 Vapor pressure of crude oils is of importance to the crude producer and the refiner for general handling and initial refinery treatment.

4.4 Vapor pressure is also used as an indirect measure of the evaporation rate of volatile petroleum solvents.

5. Apparatus

5.1 The required apparatus for Procedures A, C, and D is

¹ This test method is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.08 on Volatility.

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² *Annual Book of ASTM Standards*, Vol 05.01.

³ *Annual Book of ASTM Standards*, Vol 05.02.

⁴ *Annual Book of ASTM Standards*, Vol 05.03.

⁵ *Annual Book of ASTM Standards*, Vol 14.03.

described in Annex A1. Apparatus for Procedure B is described in Annex A2.

6. Hazards

6.1 Gross errors can be obtained in vapor pressure measurements if the prescribed procedure is not followed carefully. The following list emphasizes the importance of strict adherence to the precautions given in the procedure:

6.1.1 *Checking the Pressure Gage*—Check all gages against a pressure measuring device (see A1.6) after each test to ensure higher precision of results (see 11.4). Read the gage while in a vertical position and after tapping it lightly.

6.1.2 *Checking for Leaks*—Check all apparatus before and during each test for both liquid and vapor leaks (see Note 7).

6.1.3 *Sampling*—Because initial sampling and the handling of samples will greatly affect the final results, employ the utmost precaution and the most meticulous care to avoid losses through evaporation and even slight changes in composition (see Section 7 and 11.1). In no case shall any part of the Reid apparatus itself be used as the sample container prior to actually conducting the test.

6.1.4 *Purging the Apparatus*—Thoroughly purge the pressure gage, the liquid chamber, and the vapor chamber to be sure that they are free of residual sample. This is most conveniently done at the end of the test in preparation for the next test (see 11.5 and 14.5).

6.1.5 *Coupling the Apparatus*—Carefully observe the requirements of 11.2.

6.1.6 *Shaking the Apparatus*—Shake the apparatus vigorously as directed to ensure equilibrium.

7. Sampling

7.1 The extreme sensitivity of vapor pressure measurements to losses through evaporation and the resulting changes in composition is such as to require the utmost precaution and the most meticulous care in the handling of samples. The provisions of this section shall apply to all samples for vapor pressure determinations, except as specifically excluded for samples having vapor pressures above 180 kPa (26 psi); see Section 18.

7.2 Sampling shall be done in accordance with Practice D 4057.

7.3 *Sample Container Size*—The size of the sample container from which the vapor pressure sample is taken shall be 1 L (1 qt). It shall be 70 to 80 % filled with sample.

7.3.1 The present precision statement has been derived using samples in 1-L (1-qt) containers. However, samples taken in containers of other sizes as prescribed in Practice D 4057 can be used if it is recognized that the precision could be affected. In the case of referee testing, the 1-L (1-qt) sample container shall be mandatory.

7.4 The Reid vapor pressure determination shall be performed on the first test specimen withdrawn from the sample container. The remaining sample in the container cannot be used for a second vapor pressure determination. If necessary, obtain a new sample.

7.4.1 Protect samples from excessive heat prior to testing.

7.4.2 Do not test samples in leaky containers. They should be discarded and new samples obtained.

7.5 *Sampling Handling Temperature*—In all cases, cool the sample container and contents to 0 to 1°C (32 to 34°F) before the container is opened. Sufficient time to reach this temperature shall be ensured by direct measurement of the temperature of a similar liquid in a like container placed in the cooling bath at the same time as the sample.

8. Report

8.1 Report the result observed in 11.4 or 14.4, after correcting for any difference between the gage and the pressure measuring device (see A1.6), to the nearest 0.25 kPa (0.05 psi) as the Reid vapor pressure.

9. Precision and Bias

9.1 The following criteria are to be used for judging the acceptability of results (95 % confidence):

9.1.1 *Repeatability*— The difference between successive test results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the following value only in one case in twenty.

Procedure	Range		Repeatability		
	kPa	psi	kPa	psi	
A Gasoline	35–100	5–15	3.2	0.46	Note 3
B Gasoline	35–100	5–15	1.2	0.17	Note 3
A	0–35	0–5	0.7	0.10	Note 4
A	110–180	16–26	2.1	0.3	Note 4
C	>180	>26	2.8	0.4	Note 4
D Aviation Gasoline	50	7	0.7	0.1	Note 4

9.1.2 *Reproducibility*— The difference between two, single and independent results, obtained by different operators working in different laboratories on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the following value only in one case in twenty.

Procedure	Range		Reproducibility		
	kPa	psi	kPa	psi	
A Gasoline	35–100	5–15	5.2	0.75	Note 3
B Gasoline	35–100	5–15	4.5	0.66	Note 3
A	0–35	0–5	2.4	0.35	Note 4
A	110–180	16–26	2.8	0.4	Note 4
C	>180	>26	4.9	0.7	Note 4
D Aviation Gasoline	50	7	1.0	0.15	Note 4

NOTE 3—These precision values are derived from a 1987 cooperative program⁶ and the current Committee D-2 Statistical Method RR:D02-1007.

NOTE 4—These precision values were developed in the early 1950's prior to the current statistical evaluation method.

9.2 Bias:

9.2.1 *Absolute Bias*— Since there is no accepted reference material suitable for determining the bias for this test method, bias cannot be determined. The amount of bias between this test vapor pressure and true vapor pressure is unknown.

9.2.2 *Relative Bias*— There is no statistically significant bias between Procedures A and B for gasolines as determined in the last cooperative test program.

⁶ The results of the cooperative test program from which these values have been derived are filed at ASTM Headquarters. Request RR:D02-1245.

PROCEDURE A
FOR PETROLEUM PRODUCTS HAVING REID
VAPOR PRESSURES BELOW
180 kPa (26 psi)

10. Preparation for Test

10.1 *Verification of Sample Container Filling*—With the sample at a temperature of 0 to 1°C, take the container from the cooling bath or refrigerator and wipe dry with absorbent material. If the container is not transparent, unseal it, and using a suitable gage, confirm that the sample volume equals 70 to 80 % of the container capacity (see Note 5). If the sample is contained in a transparent glass container, verify that the container is 70 to 80 % full by suitable means (see Note 5).

NOTE 5—For non-transparent containers, one way to confirm that the sample volume equals 70 to 80 % of the container capacity is to use a dipstick that has been pre-marked to indicate the 70 and 80 % container capacities. The dipstick should be of such material that it shows wetting after being immersed and withdrawn from the sample. To confirm the sample volume, insert the dipstick into the sample container so that it touches the bottom of the container at a perpendicular angle, before removing the dipstick. For transparent containers, using a marked ruler or by comparing the sample container to a like container that has the 70 and 80 % levels clearly marked, has been found suitable.

10.1.1 Discard the sample if its volume is less than 70 % of the container capacity.

10.1.2 If the container is more than 80 % full, pour out enough sample to bring the container contents within the 70 to 80 % range. Under no circumstances shall any sample poured out be returned to the container.

10.1.3 Reseal the container, if necessary, and return the sample container to the cooling bath.

10.2 Air Saturation of Sample in Sample Container:

10.2.1 *Non-transparent Containers*—With the sample again at a temperature between 0 and 1°C, take the container from the cooling bath, wipe it dry with an absorbent material, remove the cap momentarily taking care that no water enters, reseal, and shake vigorously. Return it to the cooling bath for a minimum of 2 min.

10.2.2 *Transparent Containers*—Since 10.1 does not require that the sample container be opened to verify the sample capacity, it is necessary to unseal the cap momentarily before resealing it so that samples in transparent containers are treated the same as samples in non-transparent containers. After performing this task, proceed with 10.2.1.

10.2.3 Repeat 10.2.1 twice more. Return the sample to the bath until the beginning of the procedure.

10.3 *Preparation of Liquid Chamber*—Completely immerse the open liquid chamber in an upright position and the sample transfer connection (see Fig. A1.2) in a bath at a temperature between 0 and 1°C (32 and 34°F) for at least 10 min.

10.4 *Preparation of Vapor Chamber*—After purging and rinsing the vapor chamber and pressure gage in accordance with 11.5, connect the gage to the vapor chamber. Immerse the vapor chamber to at least 25.4 mm (1 in.) above its top in the water bath maintained at $37.8 \pm 0.1^\circ\text{C}$ ($100 \pm 0.2^\circ\text{F}$) for not less than 10 min just prior to coupling it to the liquid chamber. Do not remove the vapor chamber from the bath until the liquid chamber has been filled with sample, as described in 11.1.

11. Procedure

11.1 *Sample Transfer*—Remove the sample from the cooling bath, uncap, and insert the chilled transfer tube (see Fig. 1). Remove the liquid chamber from the cooling bath, and place the chamber in an inverted position over the top of the transfer tube. Invert the entire system rapidly so that the liquid chamber is upright with the end of the transfer tube approximately 6 mm (0.25 in.) from the bottom of the liquid chamber. Fill the chamber to overflowing (see Note 6). Withdraw the transfer tube from the liquid chamber while allowing the sample to continue flowing up to complete withdrawal.

NOTE 6—**Precaution:** In addition to other precautions, make provision for suitable containment and disposal of the overflowing sample to avoid fire hazard.

11.2 *Assembly of Apparatus*—Immediately remove the vapor chamber from the water bath and couple the filled liquid chamber to the vapor chamber as quickly as possible without spillage. When the vapor chamber is removed from the water bath, connect it to the liquid chamber without undue movement that could promote exchange of room temperature air with the 37.8°C (100°F) air in the chamber. Not more than 10 s shall elapse between removing the vapor chamber from the water bath and completion of the coupling of the two chambers.

11.3 *Introduction of the Apparatus into Bath*—Turn the assembled apparatus upside down and allow all the sample in the liquid chamber to drain into the vapor chamber. With the apparatus still inverted, shake it vigorously eight times up and down. With the gage end up, immerse the assembled apparatus in the bath, maintained at $37.8 \pm 0.1^\circ\text{C}$ ($100 \pm 0.2^\circ\text{F}$), in an inclined position so that the connection of the liquid and vapor chambers is below the water level and carefully examine for leaks (see Note 7). If no leaks are observed, further immerse the apparatus to at least 25 mm (1 in.) above the top of the vapor chamber. Observe the apparatus for leaks throughout the test and discard the test at anytime a leak is detected.

NOTE 7—Liquid leaks are more difficult to detect than vapor leaks; and because the coupling between the chambers is normally in the liquid section of the apparatus, give it particular attention.

11.4 *Measurement of Vapor Pressure*—After the assembled apparatus has been in the water bath for at least 5 min, tap the pressure gage lightly and observe the reading. Withdraw the apparatus from the bath and repeat the instructions of 11.3. At intervals of not less than 2 min, tap the gage, observe the

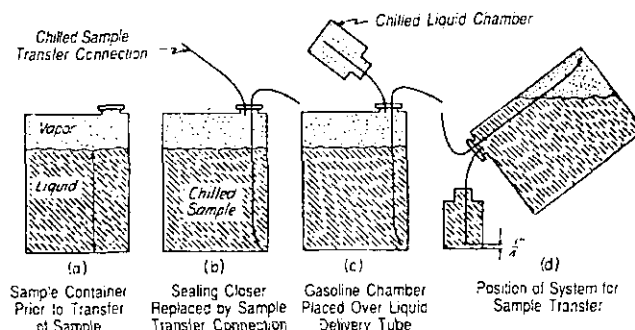


FIG. 1 Simplified Sketches Outlining Method Transferring Sample to Liquid Chamber from Open-Type Containers

reading, and repeat 11.3 until a total of not less than five shakings and gage readings have been made. Continue this procedure, as necessary, until the last two consecutive gage readings are the same, indicating that equilibrium has been attained. Read the final gage pressure to the nearest 0.25 kPa (0.05 psi) and record this value as the uncorrected vapor pressure of the sample. Without undue delay, remove the pressure gage from the apparatus (see Note 8) without attempting to remove any liquid that may be trapped in the gage, check its reading against that of the pressure measuring device (see A1.6) while both are subjected to a common steady pressure that is within 1.0 kPa (0.2 psi) of the recorded uncorrected vapor pressure. If a difference is observed between the pressure measuring device and the pressure gage readings, the difference is added to the uncorrected vapor pressure when the pressure measuring device reading is higher, or subtracted from the uncorrected vapor pressure when the pressure measuring device reading is lower, and the resulting value recorded as the Reid vapor pressure of the sample.

NOTE 8—Cooling the assembly prior to disconnecting the gage will facilitate disassembly and reduce the amount of hydrocarbon vapors released into the room.

11.5 Preparation of Apparatus for Next Test:

11.5.1 Thoroughly purge the vapor chamber of residual sample by filling it with warm water above 32°C (90°F) and allowing it to drain. Repeat this purging at least five times. Purge the liquid chamber in the same manner. Rinse both chambers and the transfer tube several times with petroleum naphtha, then several times with acetone, then blow dry using dried air. Place the liquid chamber in the cooling bath or refrigerator in preparation for the next test.

11.5.2 If the purging of the vapor chamber is done in a bath, be sure to avoid small films of floating sample by keeping the bottom and top openings of the chamber closed as they pass through the water surface.

11.5.3 *Preparation of Gage*—Disconnect the gage from its manifold connection with the pressure measuring device and remove trapped liquid in the Bourdon tube of the gage by repeated centrifugal thrusts. This is accomplished in the following manner: hold the gage between the palms of the hands with the right palm on the face of the gage and the threaded connection of the gage forward. Extend the arms forward and upward at an angle of 45°. Swing the arms rapidly downward through an arc of about 135° so that centrifugal force aids gravity in removing trapped liquid. Repeat this operation at least three times or until all liquid has been expelled from the gage. Connect the gage to the vapor chamber with the liquid connection closed and place in the 37.8°C (100°F) bath to condition for the next test. (see Note 9).

NOTE 9—**Caution:** Do not leave the vapor chamber with the gage attached in the water bath for a longer period of time than necessary to condition for the next test. Water vapor can condense in the Bourdon tube and lead to erroneous results.

PROCEDURE B FOR PETROLEUM PRODUCTS HAVING REID VAPOR PRESSURES BELOW 180 kPa (26 psi), (HORIZONTAL BATH)

12. Sampling

12.1 Refer to Section 7.

13. Preparation for Test

13.1 Refer to Section 10.

14. Procedure

14.1 *Sample Transfer*—Remove the sample from the cooling bath, uncap, and insert the chilled transfer tube (see Fig. 1). Remove the liquid chamber from the cooling bath, and place the chamber in an inverted position over the top of the transfer tube. Invert the entire system rapidly so that the liquid chamber is upright with the end of the transfer tube approximately 6 mm (0.25 in.) from the bottom of the liquid chamber. Fill the chamber to overflowing (see Note 6). Withdraw the transfer tube from the liquid chamber while allowing the sample to continue flowing up to complete withdrawal.

14.2 *Assembly of Apparatus*—Immediately remove the vapor chamber from the water bath. Disconnect the spiral tubing at the quick action disconnect. Couple the filled liquid chamber to the vapor chamber as quickly as possible without spillage or movement that could promote exchange of room temperature air with the 37.8°C (100°F) air in the vapor chamber. Not more than 10 s shall elapse between removing the vapor chamber from the water bath and completion of the coupling of the two chambers.

14.3 *Introduction of the Apparatus into the Bath*—While holding the apparatus vertically, immediately reconnect the spiral tubing at the quick action disconnect. Tilt the apparatus between 20 and 30° downward for 4 or 5 s to allow the sample to flow into the vapor chamber without getting into the tube extending into the vapor chamber from the gage, or pressure transducer. Place the assembled apparatus into the water bath maintained at $37.8 \pm 0.1^\circ\text{C}$ ($100 \pm 0.2^\circ\text{F}$) in such a way that the bottom of the liquid chamber engages the drive coupling and the other end of the apparatus rests on the support bearing. Turn on the switch to begin the rotation of the assembled liquid-vapor chambers. Observe the apparatus for leakage throughout the test (see Note 7). Discard the test at anytime a leak is detected.

14.4 *Measurement of Vapor Pressure*—After the assembled apparatus has been in the bath for at least 5 min, tap the pressure gage lightly and observe the reading. Repeat the tapping and reading at intervals of not less than 2 min, until two consecutive readings are the same. (Tapping is not necessary with the transducer model but the reading intervals should be the same.) Read the final gage or transducer pressure to the nearest 0.25 kPa (0.05 psi) and record this value as the uncorrected vapor pressure. Without undue delay, disconnect the gage from the apparatus. Connect the gage or pressure transducer to a pressure measuring device. Check its reading against that of the pressure measuring device while both are

subjected to a common steady pressure that is within 1.0 kPa (0.2 psi) of the recorded uncorrected vapor pressure. If a difference is observed between the pressure measuring device and gage or transducer readings, the difference is added to the uncorrected vapor pressure when the pressure measuring device reading is higher, or subtracted from the uncorrected vapor pressure when the pressure measuring device reading is lower, and the resulting value recorded as the Reid vapor pressure of the sample.

14.5 *Preparation of Apparatus for Next Test:*

14.5.1 Thoroughly purge the vapor chamber of residual sample by filling it with warm water above 32°C (90°F) and allowing it to drain. Repeat this purging at least five times. Purge the liquid chamber in the same manner. Rinse both chambers and the transfer tube several times with petroleum naphtha, then several times with acetone, then blow dry using dried air. Place the liquid chamber in the cooling bath or refrigerator in preparation for the next test (see Note 9).

14.5.2 If the purging of the vapor chamber is done in a bath, be sure to avoid small films of floating sample by keeping the bottom and top openings of the chamber closed as they pass through the water surface.

14.5.3 *Preparation of Gage or Transducer*—In the correct operation of this procedure, liquid should not reach the gage or transducer. If it is observed or suspected that liquid has reached the gage, purge the gage as described in 11.5.3. The transducer has no cavity to trap liquid. Ensure that no liquid is present in the T handle fitting or spiral tubing by forcing a stream of dry air through the tubing. Connect the gage or transducer to the vapor chamber with the liquid connection closed and place in the 37.8°C (100°F) bath to condition for the next test.

**PROCEDURE C
FOR PETROLEUM PRODUCTS HAVING REID
VAPOR PRESSURES ABOVE
180 kPa (26 psi)**

15. Introduction

15.1 With products having vapor pressure over 180 kPa (26 psi) see Note 10), the procedure described in Sections 7-11 is hazardous and inaccurate. Consequently, the following sections define changes in apparatus and procedure for the determinations of vapor pressures above 180 kPa. Except as specifically stated, all the requirements of Sections 1-11 shall apply.

NOTE 10—If necessary, either Procedure A or B can be used to determine if the vapor pressure of a product is above 180 kPa.

16. Apparatus

16.1 Apparatus as described in Annex A1 using the liquid chamber with two openings.

16.2 *Pressure Gage Calibration*—A dead-weight tester (see A1.7) can be used in place of the mercury manometer as a pressure measuring device (see A1.6) for checking gage readings above 180 kPa (26 psi). In 6.1.1, 8.1, 11.4, and 11.5.3 where the words *pressure measuring device* and *pressure measuring device reading* appear, include as an alternative *dead-weight tester* and *calibrated gage reading* respectively.

17. Hazards

17.1 The precaution in 6.1.6 shall not apply.

18. Sampling

18.1 Sections 7.3, 7.3.1, 7.4 and 7.5 shall not apply.

18.2 *Sample Container Size*—The size of the sample container from which the vapor pressure sample is taken shall not be less than 0.5 L (1 pt) liquid capacity.

19. Preparation for Test

19.1 Paragraphs 10.1 and 10.2 shall not apply.

19.2 Any safe method of displacement of the test sample from the sample container that ensures filling the liquid chamber with a chilled, unweathered sample may be employed. The following, 19.3-19.5, describe displacement by self-induced pressure.

19.3 Maintain the sample container at a temperature sufficiently high to maintain superatmospheric pressure but not substantially over 37.8°C (100°F).

19.4 Completely immerse the liquid chamber, with both valves open, in the water cooling bath for a sufficient length of time to allow it to reach the bath temperature of 0 to 4.5°C (32 to 40°F).

19.5 Connect a suitable ice-cooled coil to the outlet valve of the sample container (see Note 11).

NOTE 11—A suitable ice-cooled coil can be prepared by immersing a spiral of approximately 8 m (25 ft) of 6.35-mm (0.25-in.) copper tubing in a bucket of ice water.

20. Procedure

20.1 Paragraphs 11.1 and 11.2 shall not apply.

20.2 Connect the 6.35-mm (0.25-in.) valve of the chilled liquid chamber to the ice-cooled coil. With the 12.7-mm (0.5 in.) valve of the liquid chamber closed, open the outlet valve of the sample container and the 6.35-mm (0.25-in.) valve of the liquid chamber. Open the liquid chamber 12.7-mm (0.5-in.) valve slightly and allow the liquid chamber to fill slowly. Allow the sample to overflow until the overflow volume is 200 mL or more. Control this operation so that no appreciable drop in pressure occurs at the liquid chamber 6.35-mm (0.25-in.) valve. In the order named, close the liquid chamber 12.7-mm (0.5-in.) and 6.35-mm (0.25-in.) valves; and then close all other valves in the sample system. Disconnect the liquid chamber and the cooling coil.

NOTE 12—**Warning:** Combustible. Keep away from heat, sparks, and open flame. Keep container closed. Use only with adequate ventilation. Avoid prolonged breathing of vapor or spray mist. Avoid prolonged, repeated contact with skin.

NOTE 13—**Precaution:** In addition to other precautions, provide a safe means of disposal of liquid and vapor escaping during this whole operation.

20.2.1 To avoid rupture because of the liquid-full condition of the liquid chamber, the liquid chamber must be quickly attached to the vapor chamber and the 12.7-mm (0.5-in.) valve opened.

20.3 Immediately attach the liquid chamber to the vapor chamber and open the liquid chamber 12.7-mm (0.5-in.) valve. Not more than 25 s shall pass in completing the assembly of the apparatus after filling the liquid chamber, using the following sequence of operations:

20.3.1 Remove the vapor chamber from the water bath.

20.3.2 Connect the vapor chamber to the liquid chamber.

20.3.3 Open the liquid chamber 12.7-mm (0.5-in.) valve.

20.4 If a dead-weight tester is used instead of the mercury manometer as a pressure measuring device (see 16.2), apply the calibration factor in kilopascals (pounds-force per square inch) established for the pressure gage to the uncorrected vapor pressure. Record this value as the calibrated gage reading and use in Section 8 in place of the pressure measuring device reading.

**PROCEDURE D
FOR AVIATION GASOLINES
APPROXIMATELY 50 kPa (7 psi) REID VAPOR
PRESSURE**

21. Introduction

21.1 The following sections define changes in apparatus and procedure for the determination of the vapor pressure of aviation gasoline. Except as specifically stated hererin, all the requirements set forth in Sections 1-11 shall apply.

22. Apparatus

22.1 *Ratio of Vapor and Liquid Chambers*—The ratio of the volume of the vapor chamber to the volume of the liquid chamber shall be between the limits of 3.95 and 4.05 (see A1.1.4).

23. Sampling

23.1 Refer to Section 7.

24. Preparation for Test

24.1 *Checking the Pressure Gage or Pressure Transducer*—The gage shall be checked at 50 kPa (7 psi) against a mercury column (or some other calibrated pressure measuring device) before each vapor pressure measurement to ensure that it conforms to the requirements of A1.2. This preliminary check shall be made in addition to the final gagecomparison specified in 11.4 or 14.4.

25. Procedure

25.1 Refer to Section 11.

26. Keywords

26.1 crude oils; gasoline; Reid vapor pressure; spark-ignition engine fuel; vapor pressure; volatility

ANNEXES

(Mandatory Information)

A1. APPARATUS FOR VAPOR PRESSURE TEST PROCEDURE A

A1.1 *Reid Vapor Pressure Apparatus*, consisting of two chambers, a vapor chamber (upper section) and a liquid chamber (lower section), shall conform to the following requirements:

A1.1.1 *Vapor Chamber*— The upper section or chamber, as shown in Fig. A1.1, shall be a cylindrical vessel having the inside dimensions of 51 ± 3 mm ($2 \pm \frac{1}{8}$ in.) in diameter and 254 ± 3 mm ($10 \pm \frac{1}{8}$ in.) in length, with the inner surfaces of the ends slightly sloped to provide complete drainage from either end when held in a vertical position. On one end of the vapor chamber, a suitable gage coupling with an internal diameter of not less than 4.7 mm ($\frac{3}{16}$ in.) shall be provided to receive the 6.35-mm ($\frac{1}{4}$ -in.) gage connection. In the other end of the vapor chamber, an opening approximately 12.7 mm ($\frac{1}{2}$ in.) in diameter shall be provided for coupling with the liquid chamber. Care shall be taken that the connections to the openings do not prevent the chamber from draining completely.

A1.1.2 *Liquid Chamber—One Opening*—The lower section or liquid chamber, as shown in Fig. A1.1, shall be a cylindrical vessel of the same inside diameter as the vapor chamber and of such a volume that the ratio of the volume of the vapor chamber to the volume of the liquid chamber shall be between 3.8 and 4.2. (see A1.1.3). In one end of the liquid chamber an opening of approximately 12.7 mm ($\frac{1}{2}$ in.) in diameter shall be

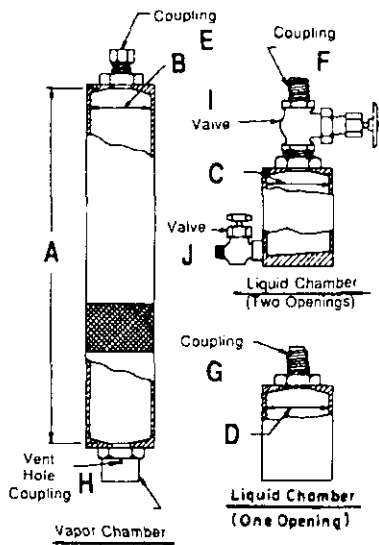
provided for coupling with the vapor chamber. The inner surface of the coupling end shall be sloped to provide complete drainage when inverted. The other end of the chamber shall be completely closed.

NOTE A1.1—**Caution:** To maintain the correct volume ratio between the vapor chamber and the liquid chamber, paired chambers shall not be interchanged without recalibration to ascertain that the volume ratio is within the required limits.

A1.1.3 The ratio of paired vapor and liquid chambers to be used for aviation gasoline testing shall be between 3.95 and 4.05.

A1.1.4 *Liquid Chamber—Two Openings*—For sampling from closed vessels, the liquid section of liquid chamber, as shown in Fig. A1.1, shall be essentially the same as the liquid chamber described in A1.1.2, except that a 6.35-mm (0.25-in.) valve shall be attached near the bottom of the liquid chamber and a 12.7-mm (0.5-in.) straight-through, full-opening valve shall be introduced in the coupling between the chambers. The volume of the liquid chamber, including only the capacity enclosed by the valves, shall fulfill the volume ratio requirements as set forth in A1.1.2.

A1.1.5 In determining the capacities for the two-opening liquid chamber (Fig. A1.1), the capacity of the liquid chamber shall be considered as that below the 12.7-mm (0.5-in.) valve



DIMENSIONS OF VAPOR PRESSURE APPARATUS

Key	Description	mm	in.
A	Vapor chamber, length	254 ± 3	10 ± 1/16
B, C, D	Vapor and gasoline chambers, Liquid ID	51 ± 3	2 ± 1/16
E	Coupling, ID min	4.7	3/16
F, G	Coupling, OD	12.7	1/2
H	Coupling, ID	12.7	1/2
I	Valve	12.7	1/2
J	Valve	6.35	1/4

FIG. A1.1 Vapor Pressure Apparatus

closure. The volume above the 12.7-mm (0.5-in.) valve closure, including the portion of the coupling permanently attached to the liquid chamber, shall be considered as a part of the vapor chamber capacity.

A1.1.6 Method of Coupling Vapor and Liquid Chambers—Any method of coupling the vapor and liquid chambers can be employed, provided that no sample is lost from the liquid chamber during the coupling operation, that no compression effect is caused by the act of coupling, and that the assembly is free of leaks under the conditions of the tests. To avoid displacement of sample during assembly, the male fitting of the coupling must be on the liquid chamber. To avoid compression of air during assembly, a vent hole must be present to ensure atmospheric pressure in the vapor chamber at the instant of sealing.

NOTE A1.2—Caution: Some commercially available apparatus do not make adequate provision for avoiding air compression effects. Before

employing any apparatus, it shall be established that the act of coupling the two chambers does not compress air in the vapor chamber. This can be accomplished by tightly stoppering the liquid chamber and coupling the apparatus in the normal manner, utilizing a 0 to 35 kPa (0 to 5 psi) gage. Any observable pressure increase on the gage is an indication that the apparatus does not adequately meet the specifications of this test method. If this problem is encountered, consult the manufacturer for a remedy.

A1.1.7 Volumetric Capacity of Vapor and Liquid Chambers—To ascertain if the volume ratio of the chambers is within the specified limits of 3.8 to 4.2 (see A1.1.3), carefully measure a quantity of water greater than will be required to fill the two chambers. (A dispensing buret is a convenient vessel for this operation.) Without spillage fill the liquid chamber completely. The difference between the original volume and the remaining volume of the measured water quantity is the volume of the liquid chamber. Without spillage couple the liquid and vapor chambers and fill the vapor chamber to the seat of the gage connection with more of the measured water. The difference between the final volume of the measured water quantity and the intermediate volume measured after ascertaining the liquid chamber volume is the volume of the vapor chamber.

A1.2 Pressure Gage—The pressure gage shall be a Bourdon type spring gage of test gage quality 100 to 150 mm (4.5 to 6.5 in.) in diameter provided with a nominal 6.35-mm (0.25-in.) male thread connection with a passageway not less than 4.7 mm (3/16 in.) in diameter from the Bourdon tube to the atmosphere. The range and graduations of the pressure gage shall be governed by the vapor pressure of the sample being tested, in accordance with Table A1.1. Only accurate gages shall be continued in use. When the gage reading differs from the pressure measuring device reading, or dead-weight tester reading when testing gages above 180 kPa (26 psi), by more than 1% of the scale range of the gage, the gage shall be considered inaccurate. For example, the calibration correction shall not be greater than 0.3 kPa (0.15 psi) for a 0 to 30-kPa (0 to 15 psi-) gage or 0.9 kPa (0.3 psi) for a 0 to 90-kPa (0 to 30-psi) gage.

NOTE A1.3—Gages 90 mm (3.5 in.) in diameter can be used in the 0 to 35 kPa (0 to 5 psi) range.

A1.3 Cooling Bath—A cooling bath shall be provided of such dimensions that the sample containers and the liquid chambers can be completely immersed. Means for maintaining the bath at a temperature between 0 and 1 (32 and 34°F) must be provided. Do not use solid carbon dioxide to cool samples in storage or in the preparation of the air saturation step.

TABLE A1.1 Pressure Gage Range and Graduations

Reid Vapor Pressure		Gage to be Used						
		Scale Range		Maximum Numbered Intervals		Maximum Intermediate Graduations		
kPa	psi	kPa	psi	kPa	psi	kPa	psi	
≤ 27.5	≤ 4	0–35	0–5	5.0	1	0.5	0.1	
20.0–75.0	3–12	0–100	0–15	15.0	3	0.5	0.1	
70.0–180.0	10–26	0–200	0–30	25.0	5	1.0	0.2	
70.0–250.0	10–36	0–300	0–45	25.0	5	1.0	0.2	
200.0–375.0	30–55	0–400	0–60	50.0	10	1.5	0.25	
≥ 350.0	≥ 50	0–700	0–100	50.0	10	2.5	0.5	

Carbon dioxide is appreciably soluble in gasoline and its use has been found to be the cause of erroneous vapor pressure data.

A1.4 *Water Bath*—The water bath shall be of such dimensions that the vapor pressure apparatus can be immersed to at least 25.4 mm (1 in.) above the top of the vapor chamber. Means for maintaining the bath at a constant temperature of $37.8 \pm 0.1^\circ\text{C}$ ($100 \pm 0.2^\circ\text{F}$) shall be provided. In order to check this temperature, the bath thermometer shall be immersed to the 37°C (98°F) mark throughout the vapor pressure determination.

A1.5 *Thermometer*—An ASTM Reid Vapor Pressure Thermometer 18C (18F) having a range from 34 to 42°C (94 to 108°F) and conforming to the requirements in Specification E 1.

A1.6 *Pressure Measuring Device*—A pressure measuring device having a range suitable for checking the pressure gage employed shall be used. The pressure measuring device shall have a minimum accuracy of 0.5 kPa (0.07 psi) with increments no larger than 0.5 kPa (0.07 psi).

A1.6.1 When a mercury manometer is not used as the pressure measuring device, the calibration of the pressure measuring device employed shall be periodically checked (with traceability to a nationally recognized standard) to ensure that the device remains within the required accuracy specified in A1.6.

A1.7 *Dead-Weight Tester*—A dead-weight tester can be used in place of the mercury manometer if used as the pressure measuring device (A1.6) for checking gage readings above 180 kPa (26 psi).

A1.8 *Sample Transfer Connection*—This is a device for removing liquid from the sample container without interfering with the vapor space. The device consists of two tubes inserted into a two-holed stopper of appropriate dimensions to fit the opening of the sample container. One of the tubes is short for the delivery of the sample, and the other is long enough to reach the bottom corner of the sample container. Fig. A1.2 shows a suitable arrangement.

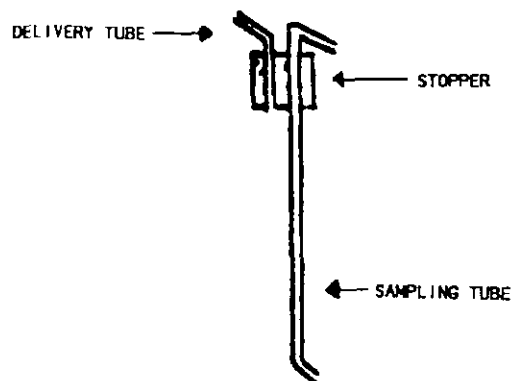


FIG. A1.2 Sample Transfer Connection

A2. APPARATUS FOR VAPOR PRESSURE TEST PROCEDURE B

A2.1 *Vapor Pressure Apparatus*—Refer to A1.1.1 through Note A1.1 and A1.1.6 and A1.1.7.

A2.2 *Pressure Gage*—The pressure measuring system shall be a Bourdon type spring gage, as described in A1.2 or a suitable pressure transducer and digital readout. The pressure measuring system shall be remotely mounted from the vapor pressure apparatus and terminations provided for use of a quick connection type fitting.

A2.3 *Cooling Bath*—Refer to Note A1.1

A2.4 *Water Bath*—The water bath shall be of such dimensions that the vapor pressure apparatus can be immersed in a horizontal position. Provision shall be made to rotate the apparatus on its axis 350° in one direction and then 350° in the opposite direction in repetitive fashion. Means for maintaining the bath at a constant temperature of $37.8 \pm 0.1^\circ\text{C}$ ($100 \pm 0.2^\circ\text{F}$) shall be provided. In order to check this temperature, the

bath thermometer shall be immersed to the 37°C (98°F) mark throughout the vapor pressure determination. A suitable bath is shown in Fig. A2.1 and is available commercially.

A2.5 *Thermometers*—Refer to A1.5.

A2.6 *Pressure Measuring Device*—Refer to A1.6.

A2.7 *Flexible Coupler*—A suitable flexible coupling shall be provided for connection of the rotating vapor pressure apparatus to the pressure measuring device.

A2.8 *Vapor Chamber Tube*—The vapor chamber tube of inner diameter 3 mm ($1/8$ in.) and length of 114 mm (4.5 in.) shall be inserted into the pressure measuring end of the vapor chamber to prevent liquid from entering the vapor pressure measuring connections (see Fig. A2.2).

A2.9 *Sample Transfer Connection*—Refer to A1.8.

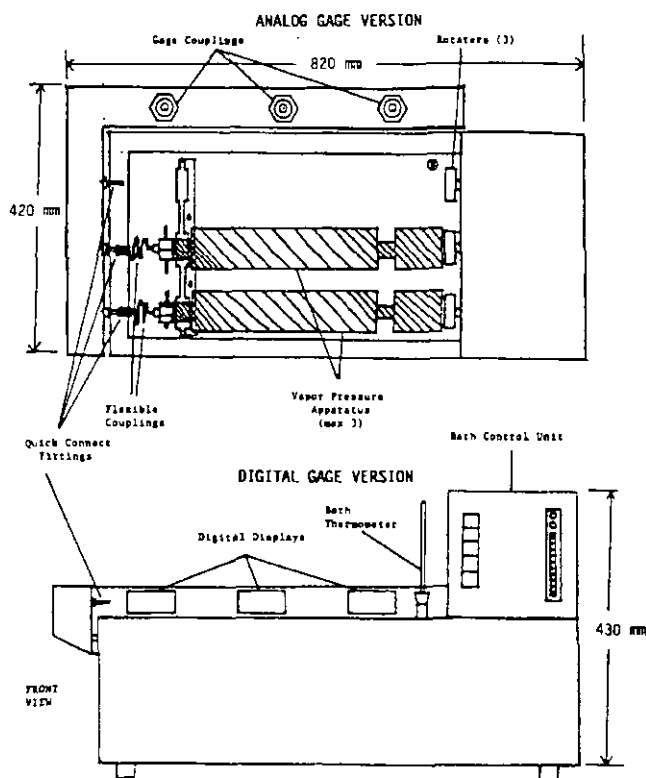


FIG. A2.1 Apparatus for Vapor Pressure, Procedure B

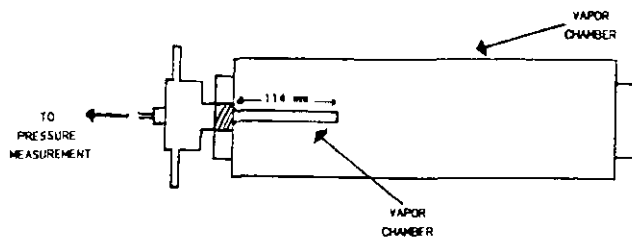


FIG. A2.2 Vapor Chamber Tube Inserted in Vapor Chamber

SUMMARY OF CHANGES

Committee D02.08 has identified the location of selected changes to this standard since the last issue (Test Method D 323-94) that may impact the use of this standard.

- (1) Updated the information in Footnote 6 to reflect current supplier.
- (2) A new Note 5 has been added after section 10.1 to provide guidance as to how to verify whether a transparent or non-transparent container is filled to between 70 and 80 % by volume of the sample container capacity.
- (3) A new paragraph, 10.1.3, has been added to explicitly state to reseal the sample container, if necessary.
- (4) A new paragraph, 10.2.1, has been added (and subsequent sections renumbered) to ensure that transparent and non-

- transparent containers are opened the same number of times prior to analysis.
- (5) A1.6 and A2.6 requirements have been changed from mercury manometer to pressure measuring device. An accuracy requirement for the pressure measuring device has also been specified. References to manometer have been replaced with pressure measuring device as appropriate throughout the method. Paragraph A1.6.1 has been added to require pressure measuring devices that are not mercury manometers to have their calibrations periodically checked (with traceability to a nationally recognized standard).

 D 323

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**Technology Assessment to Determine the Relationship of Solvent Vapor
Pressure and Mass VOC Emissions**

Attachment B

ASTM D 2369-01

**Standard Test Method for Volatile
Content of Coatings**



Standard Test Method for Volatile Content of Coatings¹

This standard is issued under the fixed designation D 2369; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

This standard has been approved for use by agencies of the Department of Defense.

1. Scope

1.1 This test method describes a procedure for the determination of the weight percent volatile content of solventborne and waterborne coatings. Test specimens are heated at $110 \pm 5^\circ\text{C}$ for 60 min.

NOTE 1—The coatings used in these round-robin studies represented air-dried, air-dried oxidizing, heat-cured baking systems, and also included multicomponent paint systems.

1.2 Sixty minutes at $110 \pm 5^\circ\text{C}$ is a general purpose test method based on the precision obtained with both solventborne and waterborne coatings (see Section 9). These coatings (single package, heat cured) are commonly applied in factories to automobiles, metal containers, flat (coil) metal and large appliances, and many other metal parts.

1.3 This test method is viable for coatings wherein one or more parts may, at ambient conditions, contain liquid coreactants that are volatile until a chemical reaction has occurred with another component of the multi-package system.

NOTE 2—Committee D-1 has run round-robin studies on volatiles of multicomponent paint systems. The only change in procedure is to premix the weighed components in the correct proportions and allow the specimens to stand at room temperature for 1 h prior to placing them into the oven.

1.4 This test method may not be applicable to all types of coatings. Other procedures may be substituted with mutual agreement between the producer and the user.

NOTE 3—If unusual decomposition or degradation of the specimen occurs during heating, the actual time and temperature used to cure the coating in practice may be substituted for the time and temperature specified in this test method, subject to mutual agreement between the producer and the user. The U.S. EPA Reference Method 24 specifies $110 \pm 5^\circ\text{C}$ for 1 h for coatings.

1.5 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use. For a specific hazard statement see 7.4.1.*

¹ This test method is under the jurisdiction of ASTM Committee D01 on Paint and Related Coatings, Materials, and Applications and is the direct responsibility of Subcommittee D01.21 on Chemical Analysis of Paints and Paint Materials.

Current edition approved Jan. 10, 2001. Published March 2001. Originally published as D 2369 – 65 T. Last previous edition D 2369 – 98.

2. Referenced Documents

2.1 ASTM Standards:

D 1193 Specification for Reagent Water²

D 3925 Practice for Sampling Liquid Paints and Related Pigmented Coatings³

E 145 Specification for Gravity-Convection and Forced-Ventilation Ovens⁴

E 180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals⁵

2.2 Other Standards:

EPA Reference Method 24—Determination of Volatile Matter Content, Density, Volume Solids, and Weight Solids of Surface Coatings⁶

3. Summary of Test Method

3.1 A designated quantity of coating specimen is weighed into an aluminum foil dish containing 3 mL of an appropriate solvent, dispersed, and heated in an oven at $110 \pm 5^\circ\text{C}$ for 60 min. The percent volatile is calculated from the loss in weight.

4. Significance and Use

4.1 This test method is the procedure of choice for determining volatiles in coatings for the purpose of calculating the volatile organic content in coatings under specified test conditions. The weight percent solids content (nonvolatile matter) may be determined by difference. This information is useful to the paint producer and user and to environmental interests for determining the volatiles emitted by coatings.

5. Apparatus

5.1 *Analytical Balance*, capable of weighing ± 0.1 g.

5.2 *Aluminum Foil Dishes*, 58 mm in diameter by 18 mm high with a smooth (planar) bottom surface. Precondition the dishes for 30 min in an oven at $110 \pm 5^\circ\text{C}$ and store in a desiccator prior to use. Use tongs or rubber gloves, or both, to handle the dishes.

5.3 *Forced Draft Oven*, Type IIA or Type IIB as specified in

² *Annual Book of ASTM Standards*, Vol 11.01.

³ *Annual Book of ASTM Standards*, Vol 06.01.

⁴ *Annual Book of ASTM Standards*, Vol 14.04.

⁵ *Annual Book of ASTM Standards*, Vol 15.05.

⁶ Available from Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402.

Specification E 145. The oven must be operating in accordance with Specification E 145, since it is important to have proper air flow and good temperature control to ensure good precision.

NOTE 4—Be sure the shelves are level and dampers are open.

5.4 *Syringe*, 1-mL without needle, but equipped with caps, capable of properly dispensing the coating under test, at a sufficient rate so that the specimen can be dissolved in the solvent.

NOTE 5—Disposable syringes with caps are recommended.

5.5 *Paper Clips*.

6. Reagents

6.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.⁷ Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

6.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean Type II of Specification D 1193.

6.3 *Toluene*, water or appropriate solvent.

7. Procedure

7.1 Take a representative sample of the liquid coatings in accordance with Practice D 3925. Mix thoroughly before taking specimens for individual tests. If air bubbles become entrapped, stir by hand, until the air has been removed.

NOTE 6—For waterborne paint systems it is recommended that they be stirred by hand.

NOTE 7—Paint samples tend to settle in the syringe. Obtain a freshly stirred sample for each test run.

7.2 Using a syringe weigh to 0.1 mg, by difference, the correct specimen weight according to the following:

Expected % Nonvolatile	Expected % Volatile	Specimen Weight, g
60 % or more	40 % or less	0.3 ± 0.1
Less than 60 %	more than 40 %	0.5 ± 0.1

The specimen is added to a tared aluminum foil dish (W_1) into which has been added 3 ± 1 mL of suitable solvent (6.2 or 6.3). Add the specimen dropwise, shaking (swirling) the dish to disperse the specimen completely in the solvent. If the material forms a lump that cannot be dispersed, discard the specimen and prepare a new one.

NOTE 8—Draw the specimen into the syringe. Remove the syringe from the specimen, pull the plunger tip up 6.4 mm ($\frac{1}{4}$ in.) in order to pull the specimen away from the neck of the syringe. Wipe the outer surface of the syringe to remove excess material and cap the syringe. Weigh to the

nearest 0.1 mg. After dispensing the specimen, do not wipe the tip of the syringe. Remove the specimen from the neck of the syringe by pulling up the plunger. Cap and reweigh to the nearest 0.1 mg.

NOTE 9—To facilitate dispersing the sample completely in the solvent, a metal paper clip may be placed (partially unfolded to use as a stirrer) in the preconditioned aluminum dish before weighing. The clip may then be used as a stirrer to completely disperse the specimen into the solvent. Be sure to leave the paper clip in the dish throughout the remainder of the procedure (through 7.5).

7.2.1 Similarly prepare a duplicate.

7.2.2 The result obtained is based on the mean of the results obtained in 7.2 and 7.2.1.

NOTE 10—Use disposable (no talc) rubber gloves or polyethylene to handle the syringe.

NOTE 11—If the specimen cannot be dispersed in the solvents listed (6.2 or 6.3), a compatible solvent may be substituted provided it is no less volatile than 2-ethoxyethyl acetate.

7.3 For multicomponent systems, weigh the components in the proper proportion into containers that can be capped. Mix the components together immediately, weigh the appropriate sample size from the table in 7.2, as specified into the aluminum weighing dishes containing 3 ± 1 mL of a suitable solvent. After dispersing, allow to stand for 1 h at room temperature (induction period) before placing the dishes into the oven.

NOTE 12—Other induction periods are used. See U.S. EPA Reference Method 24.

7.4 Heat the aluminum foil dishes containing the dispersed specimens in the forced draft oven (5.3) for 60 min at $110 \pm 5^\circ\text{C}$.

7.4.1 **Warning:** In addition to other precautions, provide adequate ventilation, consistent with accepted laboratory practice, to prevent solvent vapors from accumulating to a dangerous level.

7.5 Remove the dishes from the oven, place immediately in a desiccator, cool to ambient temperature, and weigh to 0.1 mg.

8. Calculation

8.1 Calculate the percent volatile matter, V , in the liquid coating as follows:

$$V_A = 100 - [((W_2 - W_1)/S_A) \times 100] \quad (1)$$

where:

V_A = % volatiles (first determination),

W_1 = weight of dish,

W_2 = weight of dish plus specimen after heating,

S_A = specimen weight, and

V_B = % volatiles (duplicate determination, calculate in same manner as V_A).

$$V = (V_A + V_B)/2 \quad (2)$$

8.2 Report V , the mean of the duplicate determination if relative percent difference is 1.5 % or less. If relative difference between V_A and V_B is greater than 1.5 %, repeat the duplicate determinations.

8.3 The percent of nonvolatile matter, N , in the coating may be calculated by difference as follows:

$$N = (N_A + N_B)/2 \quad (3)$$

⁷ *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

where:

$$N_A = 100 - V_{A_1} \text{ and}$$

$$N_B = 100 - V_{B_1}$$

N_A represents first determination and N_B represents duplicate determination.

9. Precision and Bias

9.1 The precision estimated for tests at 60 min at $110 \pm 5^\circ\text{C}$ are based on an interlaboratory study⁸ in which 1 operator in each of 15 laboratories analyzed in duplicate on 2 different days 7 samples of waterborne paints and 8 samples of solventborne paints containing between 35 and 72 % volatile material. The paints were commercially supplied. The results were analyzed statistically in accordance with Practice E 180. The within-laboratory coefficient of variation was found to be 0.5 % relative at 213 df and the between-laboratories coefficient of variation was 1.7 % relative at 198 df. Based on these coefficients, the following criteria should be used for judging the acceptability of results at the 95 % confidence level.

9.1.1 *Repeatability*—Two results, each the mean of duplicate determinations, obtained by the same operator on different days should be considered suspect if they differ by more than 1.5 % relative.

9.1.2 *Reproducibility*—Two results, each the mean of duplicate determinations, obtained by operators in different laboratories should be considered suspect if they differ by more than 4.7 % relative.

9.2 *Bias*—Bias has not been determined.

9.3 The precision results for multicomponent systems are based on an interlaboratory study in which one operator in each of five laboratories analyzed in duplicate on two different days, four samples of commercially supplied solventborne and waterborne multicomponent systems. The results were analyzed statistically in accordance with Practice E 180.

9.3.1 *Repeatability for Solventborne Multicomponent Systems*:

Coefficient of variation	0.5 %
Degrees of freedom	6
Factor (based on 95 % confidence level)	3.46
Precision	1.74 %

Two results, each the mean of duplicate determinations obtained by the same operator on different days, should be considered suspect if they vary by more than 1.74 % relative.

9.3.2 *Reproducibility for Solventborne Multicomponent Systems*:

Coefficient of variation	1.46 %
Degrees of freedom	5
Factor (based on 95 % confidence level)	3.46
Precision	5.31 %

Two results, each the mean of duplicate determinations obtained by operators in different laboratories, should be considered suspect if they vary by more than 5.31 % relative.

9.3.3 *Repeatability for Waterborne Multicomponent Systems*:

Coefficient of variation	0.53 %
Degrees of freedom	6
Factor (based on 95 % confidence level)	3.46
Precision	1.84 %

Two results, each the mean of duplicate determinations obtained by the same operator on different days, should be considered suspect if they vary by more than 1.84 % relative.

9.3.4 *Reproducibility for Waterborne Multicomponent Systems*:

Coefficient of variation	0.94 %
Degrees of freedom	5
Factor (based on 95 % confidence level)	3.64
Precision	3.43 %

Two results, each the mean of duplicate determinations obtained by operators in different laboratories, should be considered suspect if they vary by more than 3.43 % relative.

9.4 *Bias*—Since there is no accepted standard for volatile content in coatings, bias cannot be determined.

10. Keywords

10.1 multicomponent paints; nonvolatile determination; VOC baking temperature; VOC in paints; volatile determination; volatiles

⁸ Supporting data are available from ASTM Headquarters. Request RR: D01-1026.

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**Technology Assessment to Determine the Relationship of Solvent Vapor
Pressure and Mass VOC Emissions**

Attachment C

ASTM D 1475-98

**Standard Test Method for Density of Liquid Coatings,
Inks, and Related Products**



Standard Test Method For Density of Liquid Coatings, Inks, and Related Products¹

This standard is issued under the fixed designation D 1475; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

This standard has been approved for use by agencies of the Department of Defense.

1. Scope

1.1 This test method covers the measurement of density of paints, inks, varnishes, lacquers, and components thereof, other than pigments, when in fluid form.

1.2 For higher precision when working with nonpigmented materials (drying oils, varnishes, resins and related materials), Test Method D 1963 can be used to determine specific gravity and, thence, density.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* A specific precaution statement is given in 8.1.1.1.

2. Referenced Documents

2.1 ASTM Standards:

D 1193 Specification for Reagent Water²

D 1963 Test Method for Specific Gravity of Drying Oils, Varnishes, Resins and Related Materials at 25/25°C³

D 4052 Test Method for Density and Relative Density of Liquids by Digital Density Meter⁴

E 180 Practice for Determining the Precision of ASTM Method for Analysis and Testing of Industrial Chemicals⁵

E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method⁶

3. Terminology

3.1 Definitions:

3.1.1 *density*—the mass of a unit volume of a material at a specified temperature. In this method, it is expressed as the weight in grams per millilitre, or as the weight in pounds avoirdupois of one U. S. gallon, of the liquid at the specified temperature; in the absence of other temperature specification, 25°C is assumed.

¹ This test method is under the jurisdiction of ASTM Committee D-1 on Paint and Related Coatings, Materials, and Applications and is the direct responsibility of Subcommittee D01.24 on Physical Properties of Liquid Paints and Paint Materials.

Current edition approved Oct. 10, 1998. Published December 1998. Originally published as D 1475 – 57 T. Last previous edition D 1475 – 96.

² *Annual Book of ASTM Standards*, Vol 11.01.

³ *Annual Book of ASTM Standards*, Vol 06.03.

⁴ *Annual Book of ASTM Standards*, Vol 05.02.

⁵ *Annual Book of ASTM Standards*, Vol 15.05.

⁶ *Annual Book of ASTM Standards*, Vol 14.02.

3.1.2 *specific gravity (relative density)*—the ratio of the mass of a unit volume of a material at a stated temperature to the mass of the same volume of distilled water at the same temperature.

4. Summary of Test Method

4.1 The accurately known absolute density of distilled water at various temperatures (Table 1) is used to calibrate the volume of a container. The weight of the paint liquid contents of the same container at the standard temperature (25°C) or at an agreed-upon temperature is then determined and density of the contents calculated in terms of grams per millilitre, or pounds per gallon at the specified temperature.

5. Significance and Use

5.1 Density is weight per unit volume. It is a key property in the identification, characterization, and quality control of a wide range of materials. Density measurements in terms of weight per gallon are commonly used to check paint quality. If the density is not within specification, there is a good chance that there was a mischarge or other serious problem.

5.2 This test method is suitable for the determination of density of paint and related products and components when in liquid form. It is particularly applicable when the fluid has too high a viscosity or when a component is too volatile for a density balance determination.

5.3 This test method provides for the maximum accuracy required for hiding power determinations. It is equally suitable for work in which less accuracy is required, by ignoring the directions for recalibration and consideration of temperature differentials, and using as the container a “weight-per-gallon” cup.

5.4 Automatic equipment for measuring density is available (see Test Method D 4052) from several manufacturers. Such apparatus has been used for resins and latices as well as for oils and solvents. Before such equipment is used for a given product, results must be checked very carefully. Particularly with paints, inks, and resins, there are possibilities of gumming, fouling, and other interferences with operation.

6. Interferences

6.1 Highly viscous materials may entrap air and give erroneous low density values.

6.2 Paint or ink liquids may be trapped in the ground glass

TABLE 1 Absolute Density of Water, g/mL

°C	Density
15	0.999127
16	0.998971
17	0.998772
18	0.998623
19	0.998433
20	0.998231
21	0.998020
22	0.997798
23	0.997566
24	0.997324
25	0.997072
26	0.996811
27	0.996540
28	0.996260
29	0.995972
30	0.995684

or metal joints of the pieces of apparatus and give erroneous, high density values.

7. Apparatus

7.1 *Cup or Pycnometer*—Any metal weight-per-gallon cup or glass pycnometer may be used, provided that it may be filled readily with a viscous liquid, adjusted to exact volume, covered to exclude loss of volatile matter, and readily cleaned.

NOTE 1—For materials that contain solvents that evaporate rapidly, a glass pycnometer of the weld type, with a narrow stopper and a cover should be used.

7.2 *Thermometers*, graduated in 0.1°C, such as are supplied with glass pycnometers.

7.3 *Constant-Temperature Bath*, held at 25 ± 0.1°C is desirable.

7.4 *Laboratory Analytical Balance*.

NOTE 2—The usual weight-per-gallon cup and similar specialized pycnometers may have filled weights that exceed the capacity of the usual laboratory analytical balance. In such cases, use of a hanging pan, triple-beam balance, with scales graduated to 0.01 g has been found to provide results the mean of which was consistent with the overall precision and accuracy of the method.

7.5 *Desiccator and Desiccated Balance*, or a room of reasonably constant temperature and humidity are desirable.

8. Calibration of Cup or Pycnometer

8.1 Determine the volume of the container at the specified temperature by employing the following steps:

8.1.1 Clean and dry the container and bring it to constant weight. Chromic acid (see 8.1.1.1) or other effective glass cleaner and nonresidual solvents may be used with glass containers and solvents with metal containers. For maximum accuracy, continue rinsing, drying, and weighing until the difference between two successive weighings does not exceed 0.001 % of the weight of the container. Fingerprints on the container will change the weight and must be avoided. Record the weight, *M*, in grams.

8.1.1.1 **Precaution**—Chromic acid cleaning solution is corrosive to skin, eyes and mucous membranes and can cause severe burns. Avoid contact with eyes, skin or clothing. In making dilute solution, always add acid to water with care. Chromic acid cleaning solution is a strong oxidizer. Avoid

contact with organic or reducing substances as a fire could result. See supplier's Material Safety Data Sheet for further information. Other cleaners are much safer and may be equally effective.

8.1.2 Fill the container with reagent water conforming to Type II of Specification D 1193 at a temperature somewhat below that specified. Cap the container, leaving the overflow orifice open. Immediately remove excess overflowed water or water held in depressions by wiping dry with absorbent material. Avoid occluding air bubbles in the container.

8.1.3 Bring the container and contents to the specified temperature using the constant-temperature bath or room if necessary. This will cause further slight flow of water from the overflow orifice due to the expansion of the water with the rise of the temperature.

8.1.4 Remove the excess overflow by wiping carefully with absorbent material, avoiding wicking of water out of orifice, and immediately cap the overflow tube where such has been provided. Dry the outside of the container, if necessary, by wiping with absorbent material. Do not remove overflow that occurs subsequent to the first wiping after attainment of the desired temperature (Note 3). Immediately weigh the filled container to the nearest 0.001 % of its weight (Note 4). Record this weight, *N*, in grams.

NOTE 3—Handling the container with bare hands will increase the temperature and cause more overflow from the overflow orifice, and will also leave fingerprints; hence, handling only with tongs and with hands protected by clean, dry, absorbent material is recommended.

NOTE 4—Immediate and rapid weighing of the filled container is recommended here to minimize loss of weight due to evaporation of the water through orifices, and from overflow subsequent to the first wiping after attainment of temperature where this overflow is not retained by a cap.

8.1.5 Calculate the container volume as follows:

$$V = (N - M)/\rho \tag{1}$$

where:

- V* = volume of container, mL,
- N* = weight of container and water, g (7.1.4),
- M* = weight of dry container, g (7.1.1), and
- ρ = absolute density of water at specified temperature, g/mL (see Table 1).

8.1.6 Obtain the mean of at least three determinations.

9. Procedure

9.1 Repeat the steps in Section 8, substituting the sample for the reagent water and a suitable nonresidual solvent for the acetone or alcohol (see Note 5). Record the weight of the filled container, *W*, and the weight of the empty container, *w*, in grams.

NOTE 5—Trapping of paint or ink liquids in ground glass or metal joints is likely to result in high values of density that appear to increase with the viscosity and density of the material; such errors should be minimized by firm seating of the joints.

NOTE 6—Trapping of air bubbles results in low values for density. The tendency to trap air increases with increasing viscosity. Specimens should not be tested if they contain bubbles or foam. Slow stirring, standing, or the application of a vacuum may remove bubbles. If these do not work, a dilution may be necessary (see Appendix X1).

9.2 Calculate the density in grams per millilitre as follows:

D 1475

$$D_m = (W - w)/V \quad (2)$$

where:

D_m = density, g/mL.

9.3 Calculate the density in pounds per gallon as follows:

$$D = (W - w)K/V \quad (3)$$

where:

D = density, lb/gal,

K = 8.3454 (Note 7), and

V = volume of container, mL (see 8.1.6).

NOTE 7—The factor K , 8.3454, is calculated from volume-weight relationship as follows:

$$8.345404 = [(2.54)^3 \times (231.00)^2 / (453.59237)^2]$$

¹(2.54)³ is the conversion factor for millilitres to cubic inches.

²231.00 is the conversion factor for cubic inches to gallons.

³453.59237 is the conversion factor for grams to pounds.

10. Report

10.1 In reporting the density, state the test temperature to the nearest 0.1°C, the units, and the value calculated to three places (for example, $D = x.xxx$ lb/gal at 25°C); state the mean, the range, and the number of replicate determinations.

11. Precision and Bias

11.1 *Paints*—The precision estimates are based on an interlaboratory study in which one operator in each of six different laboratories analyzed in duplicate on two different days five samples of paint ranging in density from 8.5 to 12.5 lb/gal. The results were analyzed statistically in accordance with Practice E 180. The within-laboratory coefficient of variation was found to be 0.20 % relative with 25 df and the between-laboratory coefficient of variation was 0.61 % relative with 20 df. Based on these coefficients, the following criteria should be used for judging the acceptability of results at the 95 % confidence level:

11.1.1 *Repeatability*—Two results, each the mean of duplicate determinations, obtained by the same operator on different days should be considered suspect if they differ by more than 0.6 % relative.

11.1.2 *Reproducibility*—Two results, each the mean of duplicate determinations, obtained by operators in different laboratories should be considered suspect if they differ by more than 1.8 % relative.

11.2 *Inks*—A separate interlaboratory study of this test method was carried out for inks. In this study, one operator in each of seven laboratories made three determinations on four different paste ink samples. Paste inks were chosen because their viscosities are high and they would be expected to provide a difficult test for the method. The inks represented a density range of 8.4 to 8.9 lb/gal and exhibited viscosities ranging from a very soft news black to a relatively heavy sheet-fed offset ink. The results were analyzed statistically in accordance with Practice E 691. The within-laboratory standard deviation was 0.030 lb/gal and the pooled laboratory standard deviation was 0.045 lb/gal. Based on these values, the following criteria should be used for judging the acceptability of results at the 95 % confidence level:

11.2.1 *Repeatability*—Two results obtained by the same operator should be considered suspect if they differ by more than 0.084 lb/gal (1 %).

11.2.2 *Reproducibility*—Two results obtained by operators in different laboratories should be considered suspect if they differ by more than 0.125 lb/gal (1.5 %).

11.3 *Bias (Paint and Inks)*—Since there is no accepted reference material, bias cannot be determined.

12. Keywords

12.1 density; pycnometer; weight per gallon; weight per gallon cup

APPENDIXES

(Nonmandatory Information)

X1. DILUTING OF A MATERIAL TO IMPROVE AIR RELEASE

$$D_o = \frac{W_o}{\frac{W_o + W_d}{D_{d1}} - \frac{W_d}{D_{d2}}} \quad (X1.1)$$

X1.1 To reduce viscosity and improve air release, a known weight of a material that traps air may be diluted with a known weight of a solvent or another diluent of known density. After careful blending to achieve homogeneity and release air, the density of the diluted material is measured by the technique described in this test method. The following equation may be used to calculate the density of the original material:

where:

D_o = density of original material,

D_{d1} = density diluted measured in test,

D_{d2} = density diluent,

W_o = original weight, and

W_d = diluent weight.

X2. CENTRIFUGING OF MATERIAL TO REMOVE EXCESS AIR

X2.1 To reduce the variation in the density method, air is removed from the specimen by centrifuging the material, resulting in greater homogeneity between replicates. This greatly improves reproducibility and repeatability and results in slightly higher density readings.

X2.2 Apparatus

- X2.2.1 Centrifuge, capable of a maximum of 4000 r/min⁷,
- X2.2.2 Standard Density Cup,
- X2.2.3 Thermometer.

X2.3 Procedure

X2.3.1 Fill the centrifuge tube to the top (approximately 150 % of the density cup volume), adjust to the recommended temperature of 25°C ± 1. Place the tube in the centrifuge.

X2.3.2 Turn on the centrifuge and set the speed control to 2/3 power to attain a speed of 2700 to 3000 r/min.

X2.3.3 Continue to run for 15 to 20 s, stop the centrifuge, applying the brake as needed.

X2.3.4 Pour off the top foam layer.

X2.3.5 Transfer the specimen to a calibrated density cup and follow the procedure under Section 9.

X2.4 Precision and Bias

An interlaboratory study in one company showed that the centrifuge procedure resulted in a 2-fold improvement in repeatability and reproducibility, as well as better accuracy.

X2.4.1 *Repeatability*—Two results obtained by the same operator should be considered suspect if they differ by more than 0.0054 g/mL (0.045 lb/gal).

X2.4.2 *Reproducibility*—Two results obtained by operators in different laboratories should be considered suspect if they differ by more than 0.0080 g/L (0.067 lb/gal).

⁷ The centrifuge used in this study was a Dynac II.

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**Technology Assessment to Determine the Relationship of Solvent Vapor
Pressure and Mass VOC Emissions**

Attachment D

ASTM D 4017-96a

**Standard Test Method for Water in Paints and Paint Material
by Karl Fischer Method**



Standard Test Method for Water in Paints and Paint Materials by Karl Fischer Method¹

This standard is issued under the fixed designation D 4017; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method is applicable to all paints and paint materials, including resins, monomers, and solvents, with the exception of aldehydes and certain active metals, metal oxides, and metal hydroxides. While the evaluation was limited to pigmented products containing amounts of water in the 30 to 70 % range, there is reason to believe that higher and lower concentrations can be determined by this test method.

1.2 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* Specific hazard statements are given in Section 7.

2. Referenced Documents

2.1 ASTM Standards:

D 1193 Specification for Reagent Water²

D 3960 Practice for Determining Volatile Organic Compound (VOC) Content of Paint and Related Coatings³

E 180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial Chemicals⁴

E 203 Test Method for Water Using Karl Fischer Reagent⁴

2.2 Other Standard:

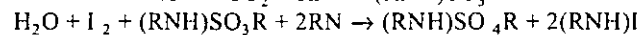
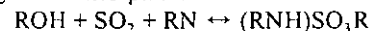
EPA Federal Reference Method 24—Determination of Volatile Matter Content, Density, Volume Solids, and Weight Solids of Surface Coatings⁵

3. Summary of Test Method

3.1 The material is dissolved in a suitable solvent, and titrated directly with standardized Karl Fischer reagent, to an electrometric end point. The sluggish reaction with water in pyridine is accelerated with a chemical catalyst, 1-ethylpiperidine.

3.1.1 Karl Fischer reagent is a mixture of iodine, amine,

sulfur dioxide, and an alcohol. In the reaction with water, iodine is reduced to hydrogen iodide. Once all the water is consumed, the appearance of free iodine is detected electrochemically and the titration is stopped. The following depicts the chemistry that takes place:



3.2 In classical Karl Fischer titrations the base used is pyridine, and the solvent either methanol or methoxy ethanol. In order to accelerate the reaction when pyridine is used, 1-ethylpiperidine is used as a catalyst/buffer. The additional buffer capacity is usually already built in to most nonpyridine based reagents such as hydranal (see Hydranal Manual).⁶

4. Significance and Use

4.1 Control of water content is often important in controlling the performance of paint and paint ingredients, and it is critical in controlling volatile organic compound (VOC) content.

4.2 Paint materials are often insoluble in common Karl Fischer solvents such as methanol. Pyridine has been found to be a nearly universal solvent for these materials; however, the Karl Fischer reaction is too slow in that solvent at room temperature. To speed it up, 1-ethylpiperidine is added at 5 % as a buffer, or “catalyst”.

4.3 For nonpyridine based reagents, a number of different solvent systems are available to increase solubility and to minimize interferences from ketones and aldehydes.

5. Apparatus

5.1 *Karl Fischer Apparatus*, manual or automatic, encompassed by the description in Test Method E 203. Apparatus should be equipped with a 25-mL buret, Class A, or equivalent.

5.2 *Syringe*, 100-μL capacity, with needle.

5.3 *Syringes*, 1-mL and 10-mL capacity, without needle, but equipped with caps.

6. Reagents

6.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that

¹ This test method is under the jurisdiction of ASTM Committee D01 on Paint and Related Coatings, Materials, and Applications and is the direct responsibility of Subcommittee D01.21 on Chemical Analysis of Paints and Paint Materials. Current edition approved July 10, 1996. Published September 1996. Originally published as D 4017 – 81. Last previous edition D 4017 – 96.

² *Annual Book of ASTM Standards*, Vol 11.01.

³ *Annual Book of ASTM Standards*, Vol 06.01.

⁴ *Annual Book of ASTM Standards*, Vol 15.05.

⁵ Available from the Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402.

⁶ Available from Hoechst Celanese Corporation, Hydranal Technical Center, U.S. Highway 43, Bucks, AL 36512.

all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.⁷ Other grades may be used, provided it is ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

TABLE 1 Specimen Guidelines

Expected water, %	Approximate Specimen Weight, g	Approximate Titrant Volume at 5 mg/mL titre, mL
0.5-1.0	5	5-10
1-3	2-5	10-20
3-10	1-2	10-20
10-30	0.4-1.0	20-25
30-70	0.1-0.4	15-25
>70	0.1	20

6.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent grade water conforming to Type II of Specification D 1193.

6.3 *Classical Karl Fischer Reagent*.⁸

6.3.1 *Nonpyridine Based Karl Fischer Reagent (KFR)*.

6.4 *Pyridine*.

6.5 *1-Ethylpiperidine*.⁹

6.6 *Hydrochloric Acid (HCl)*, concentrated.

NOTE 1—All reagents must be fresh. Do not use reagents that are more than 9 months old. Karl Fischer reagent deteriorates with age. Check expiration dates on the reagent bottle.

7. Hazards

7.1 Karl Fischer reagent contains four toxic compounds, namely iodine, sulfur dioxide, pyridine, and methanol or glycol ether. Prepare and dispense the reagent in a hood. Care must be exercised to avoid inhalation or skin contact. Following accidental contact or spillage, wash with large quantities of water.

7.2 Treat pyridine and methanol solvents with the same care as Karl Fischer reagent.

7.3 1-ethylpiperidine is of unknown toxicity and, therefore, handle with the same care as the materials listed in 7.1 and 7.2.

7.4 Handle also nonpyridine based reagents with the same care as the chemicals listed in 7.1 and 7.2.

8. Procedure

8.1 *Standardization of Karl Fischer Reagent*:

8.1.1 Add enough fresh solvent to cover the electrode tip. If using pyridine, also add 1 mL of 1-ethylpiperidine catalyst per 20 mL of pyridine. Catalyst performs best at a concentration of about 5 % of the volume present.

⁷ *Reagent Chemicals, American Chemical Society Specifications*. American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

⁸ So-K-3 available from Fischer Scientific Co., or equivalent has been found suitable for this purpose.

⁹ Use 1-ethylpiperidine, manufactured by the Aldrich Chemical Co., Milwaukee, WI 53233, for the best results.

8.1.2 Fill the 100- μ L syringe to about half full with distilled water and weigh to the nearest 0.1 mg.

8.1.3 Pretitrate the solvent to the end point indicated by the equipment manufacturer, by adding just enough Karl Fischer Reagent I (KFR) to cause the end point to hold for at least 30 s.

8.1.3.1 The use of the catalyst greatly increases the reaction rate between water and Karl Fischer reagent. To obtain reliable results, increase the electrode sensitivity and reduce titration rate to a minimum. Most instruments have controls for these functions. Consult the instructional manual for information on these controls.

8.1.4 Empty the contents of the syringe into the titrator vessel. Immediately replace the stopper of the sample port and titrate with KFR to the end point as described in 8.1.3.

8.1.5 Repeat standardization until replicate values of F agree within 1 %. Determine the mean of at least two such determinations. Carry out calculations retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after final calculations.

8.1.6 *Calculation*:

8.1.6.1 Calculate the KFR titre F as follows:

$$F = J/P \quad (1)$$

where:

J = water added, g, and

P = KFR used, mL.

The value for F should be recorded to the four significant digits and should be the mean of at least two determinations. Typical values are in the range of 0.004000 to 0.006000 g/mL.

8.2 *Analysis of Samples With More Than 0.5 % Water*:

8.2.1 The titration vessel should already contain pretitrated solvent and catalyst, as described in 8.1.1 and 8.1.3 in the standardization procedure. Best results are obtained with fresh solvent, that is, containing no previously titrated specimen in the vessel.

8.2.2 With a 1-mL or 10-mL syringe, draw the amount of material indicated in Table 1.

NOTE 2—Paint samples tend to settle in the syringe and give high percent water content. Obtain a freshly stirred or mixed specimen for each test run.

8.2.2.1 Remove the syringe from the specimen, pull the plunger out a little further, wipe the excess material off the syringe, and place a cap on the syringe tip. Weigh the filled syringe to the nearest 0.1 mg.

8.2.3 Remove the cap, and empty the syringe contents into the pretitrated solvent vessel. Pull the plunger out and replace the cap.

8.2.4 Stir rapidly for 1 to 2 min before starting titration. Some instruments can be set to do this automatically. If the specimen is still not dissolved or dispersed, continue stirring until it is dissolved, or use a different solvent in place of solvent in 8.2.1.

8.2.5 Titrate the specimen *slowly* with KFR to the end point described in 8.1.3.

8.2.6 Reweigh the emptied syringe, and calculate the specimen weight by difference.

8.2.7 *Calculation*:

8.2.7.1 Calculate the percent water L as follows:

$$L = (P \times F \times 100) / S \quad (2)$$

8.3 *Analysis of Materials With Less Than 0.5 % Water:*

8.3.1 For 0.1 to 0.5 %, follow procedure in 8.2 (1-g specimen), except substitute a 1-mL microburet for the 25-mL buret in the Karl Fischer apparatus.

8.3.2 For less than 0.1 %, use a 1-mL microburet and increase specimen size as much as needed, up to 10 g. It should be possible to measure moisture levels down to 1 ppm (0.0001 %) by this approach.

NOTE 3—Specimens with less than 0.1 % water may require special handling techniques to prevent pickup of atmospheric moisture. The precision of this test method was determined with specimens containing higher water levels.

9. Recommendations for Good Results

9.1 Make sure electrodes are clean.

9.2 Follow manufacturer's instructions to ensure that venting into the titration vessel is only through a desiccant.

9.3 Samples should be thoroughly mixed before taking a specimen.

9.4 Use an appropriate solvent/reagent for the paint/coating being analyzed. Paints and paint materials are often slow to dissolve or disperse. To ensure that all of the water is extracted into the pyridine or solvent, stir rapidly for 1 or 2 min before starting the titration.

9.5 Run the titration slowly with rapid stirring.

9.6 Throw out the first result in fresh pyridine.

9.7 Use only Aldrich's 1-ethylpiperidine.⁶ It has been found that other brands produce variable results.

9.8 For difficult-to-dissolve samples, extract the water with a suitable solvent, such as dry methanol. An example of this procedure is outlined in Appendix X1.

10. Maintenance

10.1 *Cleanup*—Clean the titration vessel by rinsing with fresh pyridine. Do not use methanol or other solvents.

10.2 *Dryness*—Check frequently to be sure that all drying tubes are in good condition and tightly connected. Replace desiccant when indicator color changes through *half of the tube*.

10.3 *Electrode Performance*—If electrode response is slug-

gish or otherwise off standard, take the following steps, in turn, to correct the problem. Test the electrode with a titration after each step, to determine if the next step is required.

10.3.1 Wipe the electrode tip with a clean paper towel.

10.3.2 Wash the electrode by dipping in concentrated hydrochloric acid for at least 1 min. Rinse first with distilled water, then with methanol.

10.3.3 Follow manufacturer's instructions on resetting end point meter.

10.3.4 Replace power source. See manual for replacement procedure.

10.3.5 Replace the electrode.

11. Precision and Bias¹⁰

11.1 The precision estimates are based on an interlaboratory study in which one operator in each of seven different laboratories analyzed in duplicate on two different days seven samples of water-based paints of various types containing between 25 to 75 % water. The results were analyzed statistically in accordance with Practice E 180. The within-laboratory coefficient of variation was found to be 0.9 % relative at 23 df, and the between-laboratory coefficient of variation was 1.9 % relative, at 18 df. Based on these coefficients, the following criteria should be used for judging the acceptability of results at the 95 % confidence level.

11.1.1 *Repeatability*—Two results, each the mean of duplicate determinations, obtained by the same operator on different days should be considered suspect if they differ by more than 3.5 % relative.

11.1.2 *Reproducibility*—Two results, each the mean of duplicate determinations, obtained by operators in different laboratories should be considered suspect if they differ by more than 5.5 % relative.

11.2 *Bias*—Bias has not been determined for this test method.

12. Keywords

12.1 Karl Fischer reagent method; moisture content; water content

¹⁰ Supporting data are available from ASTM Headquarters. Request RR:D01-1096.

APPENDICES

(Nonmandatory Information)

X1. TEST METHOD FOR KARL FISCHER WATER DETERMINATION FOR LATEX PAINTS USING EXTRACTION WITH METHANOL¹¹

X1.1 Scope

X1.1.1 If variable results are obtained with the pyridine method, the methanol extraction method is recommended.

X1.1.2 This test method is applicable to paints based on latex technology, which may not be sufficiently soluble in the solvents specified in the direct titration method. Some solvent-based paints will "ball up" in contact with methanol.

X1.1.3 *This standard does not purport to address all of the*

¹¹ Isopropanol has also been found suitable in some cases.

safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

X1.2 Referenced Documents

X1.2.1 ASTM Standards:

D 3960 Practice for Determining Volatile Organic Compound (VOC) Content of Paints and Related Coatings³

E 180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial Chemicals⁴

X1.2.2 Other Standard:

EPA Reference Method 24, Determination of Volatile Matter Content, Water Content, Density, Volume Solids, and Weight Solids of Surface Coatings⁵

X1.3 Summary of Test Method

X1.3.1 Water is quantitatively extracted from a sample with anhydrous methanol, and an aliquot is titrated for water content using commercial non-pyridine based reagents.

X1.4 Significance and Use

X1.4.1 The latex polymers in some modern coatings are not soluble, and do not readily give up their water, in pyridine or other solvents used in this test method. This procedure is designed to quantitatively extract the water, in a reasonable time, into anhydrous methanol, so it can be easily titrated. This test method may not be applicable to all coating types, and is offered as an alternative to the direct titration method in Test Method D 4017.

X1.4.2 This test method is specifically designed to obtain VOC content of waterborne coatings with minimum error.

X1.4.3 The specimen size assumes a paint that has 50 to 90 % water content. If the product being tested has a lower expected water content, larger specimens should be taken.

X1.4.4 Good results are dependent on close attention to detail. See Section X1.12, Recommendations for Good Results.

X1.4.5 For further information see Practice D 3960, EPA Reference Method 24, and Manual 4.¹²

X1.5 Apparatus

X1.5.1 Karl Fischer Titration Apparatus.¹³

X1.5.2 Disposable Syringe, 1-cc tuberculin with cap and needle.¹⁴

X1.5.3 Disposable Syringe, 1-cc tuberculin with cap and no needle.¹⁵

X1.5.4 Analytical Balance, with tare bar, readable to 0.0001 g.

X1.5.5 Sonic Bath.¹⁶

X1.5.6 Flasks, 100-mL, Class A volumetric.

X1.5.7 Pipetes, 10 mL, Class A volumetric.

X1.6 Reagents

X1.6.1 Non-Pyridine Composite Karl Fischer Reagent, (KFR)¹⁷ 5 mg/mL titre.

X1.6.2 Reagent Grade Methanol or commercial anhydrous methanol.¹⁸

X1.6.3 4A Molecular Sieve, 8–12 mesh beads (required only if drying your own material).¹⁹

X1.7 Sample Preparation

X1.7.1 Dry Methanol: Put about 200 g of 4A molecular sieve beads into a fresh 4-L bottle of reagent grade methanol and allow to stand overnight.

X1.7.2 Into two 100-mL volumetric flasks, add about 80 mL of dry methanol and stopper.

X1.7.3 Fill a 1-mL disposable syringe (the type with no needle) with freshly mixed sample of the paint to be tested. Draw back the plunger a little, wipe off the excess paint, and cap the syringe.

X1.7.4 Place the capped syringe on the balance pan and tare to zero.

X1.7.5 Remove the cap and empty the syringe into one of the flasks, being careful not to get any sample on the neck or top of the flask. Pull the plunger back a little and cap the syringe and re-stopper the flask.

X1.7.6 Place the empty, capped syringe on the balance and record the weight to the nearest 0.0001 g.

X1.7.7 Repeat X1.7.3 to X1.7.6 with a duplicate sample. Be sure to number the flasks.

X1.7.8 Add dry methanol to the mark in each flask.

X1.7.9 Place the two flasks in a sonic bath and run for 15 min. Make sure that the flasks are tightly stoppered by taping them shut with masking tape.

X1.7.10 If the flask contents are warm, cool to room temperature, or until the meniscus returns to the mark. Ensure that the flask contents are uniform by turning them upside down three or four times.

X1.8 Titre Determination Procedure

X1.8.1 Use the following instrument settings for all titrations in this test method:

END POINT DELAY: 20 s

EXTRACTION TIME: 0 min

REPORT MODE: Mass fraction, mean value

¹² MNL, 4, Manual on Determination of Volatile Organic Compound (VOC) Content in Paints, Inks, and Related Coating Products, ASTM, 1993.

¹³ The Metrohm Model E-358 was used in the development of this test method. (Brinkmann Instruments, Cantiague Rd., Westbury, NY 11590). A few references to its features are mentioned in the Procedure. Most modern Karl Fischer titrators have comparable features. This model is no longer available, but several companies, including Brinkmann, market equivalent instruments.

¹⁴ Disposable syringe, BD 9625, available from many scientific supply companies, has been found suitable for this purpose.

¹⁵ Disposable syringe, BD 9602, available from many scientific supply companies, has been found suitable for this purpose.

¹⁶ Sonic bath, VWR Catalogue No. 21812-119 or equivalent has been found suitable for this purpose. VWR Scientific, Box 232, Boston, MA 02101.

¹⁷ Hydranal® Composit 5, Catalogue No. 34801, (Crescent Chemical Co., 1324 Motor Parkway, Hauppauge, NY 11788), was used in the development of this test method. Several companies market equivalent reagents, however care should be exercised to ensure that they are equivalent. Samples containing ketones, Hydranal® Composite 5K, combined with Hydranal® Working Medium K, or equivalent reagents from other suppliers, have been found to give excellent results (see Catalogue Nos. 34816 and 34817, respectively).

¹⁸ Reagent grade methanol, VWR Catalogue No. 34801 or equivalent has been found suitable for this purpose.

¹⁹ Sieve, VWR Catalogue No. EM-MX 1583L-1 or equivalent has been found suitable for this purpose.

X1.8.2 Fill the titration vessel with enough dry methanol to cover the electrode.

X1.8.3 Titrate out the water using the non-pyridine KF reagent. On some instruments, this is done automatically in the "condition" mode.

X1.8.4 Fill a 1-cc syringe with needle with deionized water. Draw back the plunger a little, wipe off any excess water, and cap the syringe.

X1.8.5 Place the capped syringe on a 4-place analytical balance. Tare out the weight to zero.

X1.8.6 With the needle tip at the solvent surface, add 2 to 3 drops into the titration solvent. After removing the syringe, withdraw the plunger a little and cap the titration vessel.

X1.8.7 Weigh the syringe on the tared balance and record the weight to the fourth decimal. Ignore the minus sign.

X1.8.8 Titrate the water to the endpoint that holds for 20 s. Stir rapidly. Titration rate should be about 3 mL/min.

X1.8.9 *Calculation*: Most instruments will calculate the titre automatically, after entering the weight. To calculate manually, use the equation as follows:

$$\text{Titre (F)} = \frac{\text{grams of water added} \times 1000}{\text{mL KFR used}} \quad (\text{X1.1})$$

Record to the third decimal, for example 5.238 mg/mL.

X1.8.10 Repeat X1.8.3 to X1.8.8 at least two more times. Make sure that the Karl Fischer titre is the average of at least three determinations. (Many instruments will average automatically). If all values do not agree within 0.05, check the instrument. (see Appendix X1.13).

X1.9 Blank Determination

X1.9.1 The titration vessel should contain pretitrated methanol as previously described (see Appendix X1.8.2 and Appendix X1.8.3).

X1.9.2 Place the instrument in "Standby".

X1.9.3 Pipete 10.00 mL of dry methanol into the titration vessel.

X1.9.4 Titrate at the slowest rate. On some instruments, this is best done by pressing the "Condition" button. Record the volume at the end point. It will typically be in the range of 0.3 to 0.5 mL.

X1.9.5 Repeat X1.9.3 and X1.9.4 two more times. Average the three volumes.

X1.9.6 Calculate the average milligrams of water in 10.00 mL of dry methanol as follows:

$$\text{milligrams water in blank} = \text{average titration} \times F \quad (\text{X1.2})$$

For instruments with automatic blank correction in milligrams of water, enter this value in memory.

X1.9.6.1 If the instrument does not have this feature, use the average volume and calculate manually as shown under Section X1.11, Calculation

X1.9.7 The blank value will change fairly quickly, so determine this whenever a sample is run, or run it once a day if there are several samples to be done.

X1.10 Analysis of Samples

X1.10.1 The titration vessel should already contain pretitrated methanol as described under Section X1.8.

X1.10.2 Mix the volumetric flask by turning upside down once or twice.

X1.10.3 Pipete 10.00 mL into the titration vessel and titrate at about 3 mL/min.

X1.10.4 Repeat the above for the second volumetric flask.

X1.11 Calculation and Report

X1.11.1 Most instruments calculate automatically. To calculate manually, use the equation as follows:

$$\% \text{ water}^{20} = \frac{(\text{mL KFR used} - \text{mL for blank}) \times F \times 100}{\text{grams sample}} \quad (\text{X1.3})$$

Record to the second decimal, for example 70.35 %.

X1.11.2 Report the average of two results.

X1.11.3 If the results differ from each other by more than 2.3 % relative, run another set of duplicates. For example, results of 50.05 % and 51.25 % would be considered suspect.

X1.12 Precision¹⁰

X1.12.1 *Precision* —The precision estimates are based on an interlaboratory study in which one operator in each of five different laboratories analyzed in quadruplicate six samples of water-based paints of various types containing from 35 to 70 % water.¹⁰ The results were analyzed statistically in accordance with Practice E 180. The within-laboratory coefficient of variation was found to be 0.81 % relative for duplicates, at 58 df, and the between-laboratory coefficient of variation was found to be 2.55 % at 23 df. Based on these coefficients, the following criteria should be used for judging the acceptability of results at the 95 % confidence level:

X1.12.1.1 *Repeatability* —Two results obtained by the same operator should be considered suspect if they differ by more than 2.28 % relative.

X1.12.1.2 *Reproducibility*—Two results, each the mean of duplicate determinations, obtained in different laboratories, should be considered suspect if they differ by more than 7.46 % relative.

X1.12.2 *Bias* —Bias has not been determined for this test method.

X1.13 Recommendations for Good Results

X1.13.1 Clean the titration vessel by rinsing with fresh methanol. Pyridine or *n*-methyl pyrrolidone may also be used for difficult residues.

X1.13.2 Check frequently to be sure that all drying tubes are in good condition and tightly connected. Replace the desiccant when any color change is observed.

X1.13.3 To ensure against an unrepresentative sample due to settling, draw sample into the syringe right after mixing, and

²⁰ Units arrived as follows:

$$\% \text{ water} = \frac{\text{mL} \times F \times 10 \times 100}{\text{g} \times 1000} \quad (3)$$

where:

10 = dilution factor,

100 = converts into percentage, and

1000 = converts grams into milligrams.

carry out the entire operation immediately. Always use a new syringe for the second sample.

X1.13.4 Check titre and blank values at least daily.

X1.13.5 Stir rapidly and titrate slowly (~3 mL/min)

X1.13.6 The methanol solutions in the 100-mL flasks should not be allowed to stand around for a long time, as methanol will absorb water from the atmosphere, even when the flasks are stoppered, especially on humid days. All flasks and apparatus must be kept closed except when adding or withdrawing material.

X1.13.7 Problems with end points are often traceable to the electrode. If experiencing problems with repeatability or poor

end points, try the following, in order. Try a titration after each step, to see if the next one is needed:

X1.13.7.1 Wipe the electrode with a clean paper towel.

X1.13.7.2 Dip the electrode in concentrated nitric acid for 1 min. Then rinse with deionized water, followed by methanol. If any residue remains, remove with a fine abrasive such as a crocus cloth.

X1.13.7.3 Replace the electrode, and

X1.13.7.4 Check the instrument operability in accordance with the manufacturer's supplied manual.

X2. TEST METHOD FOR KARL FISCHER DETERMINATION OF WATER CONTENT IN PAINT USING A HOMOGENIZER ACCESSORY

X2.1 Scope

X2.1.1 If variable results are obtained with the pyridine method, the use of the homogenizer method is recommended.

X2.1.2 This test method is applicable to water-based paints, which may not be sufficiently soluble in the solvents specified in the pyridine titration method. Some solvent-based paints will "ball up" in contact with methanol and not disperse.

X2.1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

X2.2 Referenced Documents

X2.2.1 *ASTM Standards:*

D 3960 Practice for Determining Volatile Organic Compound (VOC) Content of Paints and Related Coatings³

E 180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial Chemicals⁴

X2.2.2 *Other Standard:*

EPA Reference Method 24, Determination of Volatile Matter Content, Water Content, Density, Volume Solids, and Weight Solids of Surface Coatings⁵

X2.3 Summary of Test Method

X2.3.1 Samples are titrated in methanol after being homogenized with a specialized accessory that quickly disperses insoluble material by reducing it to very low particle size.

X2.4 Significance and Use

X2.4.1 The latex polymers in some modern coatings are not soluble, and do not readily give up their water in pyridine or other solvents specified in Test Method D 4017. This procedure is designed to disperse insoluble specimens so to quantitatively extract the water in a reasonable time into methanol, so the water can be easily titrated. The principle is the same as in the "Methanol Extraction" procedure (Appendix X1), but with the advantage of eliminating some steps, thus saving time and eliminating sources of error. This test method may not be applicable to all coating types. It is offered only as an alternative to the Test Method D 4017 direct titration method, and the methanol extraction method in Appendix X1.

X2.4.2 This test method has been found to give precise and consistent results for water content.

X2.4.3 The specimen size assumes a paint which has 50 to 90 % water content. If the product being tested has a lower expected water content, larger specimens should be taken.

X2.4.4 Good results are dependent on close attention to detail. See Section X2.11, "Recommendations for Good Results".

X2.5 Apparatus

X2.5.1 *Karl Fischer Titration Apparatus.*²¹

X2.5.2 *Homogenizer.*²²

X2.5.3 *Disposable Syringe,*¹⁴ 1 cc tuberculin with cap and needle.

X2.5.4 *Disposable Syringe,*¹⁵ 1 cc tuberculin with cap and no needle.

X2.5.5 *Analytical Balance,* with tare bar, readable to 0.0001 g.

X2.6 Reagents

X2.6.1 *Non-Pyridine Composite Karl Fischer Reagent,*¹⁷ 5 mg/mL titre.

X2.6.2 *Reagent Grade Methanol.*¹⁸

X2.7 Titre Determination

X2.7.1 If possible, use the following instrument settings for all titrations in this test method:

Homogenizer settings: 30 s, lowest speed

Extraction Time: - 60 s, (prevents titration from starting until 30 s after homogenizer stops),

End point delay time: 20 s,

Report mode: mass fraction, mean value (to read out as percent water and average the results).

X2.7.2 Fill the titration vessel with enough methanol to cover the homogenizer blades and the electrodes with stirrer on.

²¹ The Metrohm Model E-701 was used in the development of this test method. (Brinkman Instruments, Cantiague Rd., Westbury, NY 11590). A few references to its features are mentioned in the procedure. Most modern Karl Fischer titrators have comparable features. Several companies market equivalent instruments.

²² Model No. 2000, available from Brinkmann Instruments. The homogenizer may be used with other company's titrators; however no accessory comparable to the Brinkmann Homogenizer is known to be available from other vendors.

X2.7.3 Titrate out the water using the non-pyridine composite KF titrant. On most instruments, this is done automatically in the "condition" mode.

X2.7.4 RUN A "DUMMY" TITRATION. That is, run the homogenizer for 30 s, wait 30 s, and start the titration, with NO SPECIMEN ADDED. Throw out the result.

X2.7.5 Fill a 1-cc syringe with needle with deionized water. Draw back the plunger ¼ in. (5 mm), wipe off any excess water, and cap the syringe.

X2.7.6 Place the capped syringe on a 4-place analytical balance. Tare out the weight to zero.

X2.7.7 With the needle tip at the solvent surface, add 2 to 3 drops (0.0250 to 0.0500 g) into the titration solvent. After removing the syringe, withdraw the plunger ¼ in. (5 mm) and cap the titration vessel.

X2.7.8 Weigh the syringe on the tared balance and record the weight to the fourth decimal. Ignore the minus sign.

X2.7.9 Run the homogenizer for 30 s, then wait for 30 s. (Will be done automatically on instruments that accept the above settings.) Titrate the water to the end point that holds for 20 s. Stir rapidly. Titration rate should be about 3 mL/min.

X2.7.10 *Calculation:* Most instruments will calculate the titre automatically, after entering the weight. To calculate manually, use the following equation as follows:

$$\text{Titre (F)} = \frac{\text{grams of water added} \times 1000}{\text{mL KFR used}} \quad (\text{X2.1})$$

Record to the third decimal, for example 5.238 mg/mL.

X2.7.11 REPEAT X2.7.6 TO X2.7.9 AT LEAST TWO MORE TIMES. The Karl Fischer titre should be the average of at least three determinations. (Many instruments will average automatically). If the range of values exceeds 0.1, check the instrument (see Section X1.3).

X2.8 Sample Determination

X2.8.1 If possible, set the following parameters on your instrument:

Homogenizer settings: 30 s, lowest speed

Extraction Time: - 60 s, (prevents titration from starting until homogenizer stops),

End point delay time: 20 s,

Report mode: mass fraction, mean value (to read out as percent water and average the results).

X2.8.2 Add fresh methanol to cover the homogenizer blades and the electrodes when the stirrer is on.

X2.8.3 RUN A "DUMMY" TITRATION. That is, run the homogenizer for 30 s, wait 30 s, and start the titration, with NO SPECIMEN ADDED. Throw out the result.

X2.8.4 Fill a 1-mL disposable syringe (the type with no needle) with freshly mixed sample of the paint to be tested. Draw back the plunger ¼ in. (5 mm), wipe off the excess paint, and cap the syringe.

X2.8.5 Place the capped syringe on the balance pan and tare to zero.

X2.8.6 Remove the syringe cap, and add 2 to 3 drops (equivalent to 0.0300 to 0.0500 g of water for a sample which

has about 50 % water) into the titration vessel.²³ Draw back the plunger ¼ in. (5 mm), and immediately cap the syringe and close the titration vessel.

X2.8.7 Weigh the syringe on the tared balance and record to the fourth place after the decimal. Ignore the minus sign. Transfer the weight to the titrator, if required for your instrument.

X2.8.8 Run the homogenizer for 30 s, then wait for 30 s. (Will be done automatically on instruments that accept the above settings.) Titrate the water to the end point that holds for 20 s. Stir rapidly. Initial titration rate should be about 3 mL/min.

X2.8.9 Repeat X2.8.4 to X2.8.8 for a duplicate specimen.

X2.9 Calculation and Report

X2.9.1 Calculate percent water as follows:

$$\% \text{ water} = \frac{\text{mL KFR} \times F \times 100}{\text{mg of specimen}} \quad (\text{X2.2})$$

X2.9.2 Report the average of results on two specimens.

X2.9.3 A set of duplicates with a range of more than 2.2 % relative should be considered suspect and be rerun. For example, duplicate results of 50.05 and 51.20 % would be suspect.

X2.10 Precision

X2.10.1 *Precision* —The precision estimates are based on an interlaboratory study in which one operator in each of nine different laboratories analyzed in quadruplicate six samples of water-based paints of various types containing from 35 to 70 % water.¹⁰ The results were analyzed statistically in accordance with Practice E 180. The within-laboratory coefficient of variation was found to be 0.79 % relative for duplicates, at 98 df, and the between-laboratory coefficient of variation was found to be 1.47 % at 43 df. Based on these coefficients, the following criteria should be used for judging the acceptability of results at the 95 % confidence level:

X2.10.1.1 *Repeatability* —Two results obtained by the same operator should be considered suspect if they differ by more than 2.20 % relative.

X2.10.1.2 *Reproducibility* —Two results, each the mean of duplicate determinations, obtained in different laboratories should be considered suspect if they differ by more than 4.20 % relative.

X2.10.2 *Bias* —Bias has not been determined for this test method.

X2.11 Recommendations for Good Results

X2.11.1 Clean the titration vessel by rinsing with fresh methanol. Pyridine or *n*-methyl pyrrolidone are suggested for difficult residues.

X2.11.2 Check frequently to be sure that all drying tubes are in good condition and tightly connected. Replace the desiccant when any color change is observed.

X2.11.3 To ensure against an unrepresentative sample due to settling, draw sample into the syringe right after mixing, and

²³ Other specimen sizes may be used.

carry out the entire operation immediately. Always use a new syringe for the second sample.

X2.11.4 Check titre values daily.

X2.11.5 Stir rapidly and titrate slowly (~3 mL/min).

X2.11.6 Problems with end points are often traceable to the electrode. If experiencing problems with repeatability or drifting end points, try the following steps, in order. Try a titration after each step, to see if the next one is needed:

X2.11.6.1 Wipe the electrode with a clean paper towel.

X2.11.6.2 Dip the electrode in concentrated nitric acid for 1 min. Then rinse with deionized water, followed by methanol. If any residue remains, remove with a fine abrasive such as a crocus cloth.

X2.11.6.3 Replace the electrode.

X2.11.6.4 Check the instrument operability in accordance with the manufacturer's supplied manual

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**Technology Assessment to Determine the Relationship of Solvent Vapor
Pressure and Mass VOC Emissions**

Attachment E

Measured Parameters of Solvent Samples

Results Summary
Evaporation Rate, Vapor Pressure & VOC Measurements

Product	sample weight (mg)	time to wt.=0 or k (mins.)	rate of wt. loss (mg/min)	rate of wt. loss (%w/min)	peak rate of wt. loss (%w/min)	Reid VP (psi)	evaporation rate (BuOAc=1)	VOC (g/L)
Prisco Superklene 2P	23.027	41.83	0.55	2.39	3.92	0.87	0.27	810
PriscoMRC-F	20.164	32.88	0.61	3.04	26.84	5.50	0.35	820
Prisco Powerclean VC	25.219	70.10	0.36	1.43	2.70	0.77	0.16	810
Prisco Autowash 6000	22.566	43.27	0.52	2.31	3.44	0.89	0.26	780
Prisco Autowash LA3	19.275	28.70	0.67	3.48	21.67	5.40	0.40	800
Prisco UV#8	27.623	59.28	0.47	1.69	2.65	0.62	0.19	880
Prisco Superklene 1IC	23.706	175.00	0.14	0.57	1.88	1.36	0.06	700
Star #1001	20.050	5.29	3.79	18.90	24.90	4.88	2.15	750
Star LVP-25	20.521	10.00	2.05	10.00	21.48	5.40	1.14	780
Star Ultra 2B	24.399	30.05	0.81	3.33	5.56	0.88	0.38	780
Star #250 Wash	22.071	7.02	3.14	14.25	19.26	2.26	1.62	790
2-Butoxyethanol	27.283	89.13	0.31	1.12	4.43	0.44	0.13	900
2-Propanol	21.639	7.60	2.85	13.16	16.10	2.25	1.49	780
Toluene	26.628	6.30	4.23	15.87	19.52	1.77	1.80	860
n-Butyl acetate	24.894	11.35	2.19	8.81	11.25	N/A	1.00	N/A
Mineral spirits	25.717	80.05	0.32	1.25	1.85	N/A	0.14	N/A

Methods/Materials

- 1) Vapor pressures were measured as Reid vapor pressure, dry and 100°F by ASTM D 323-99a.
- 2) VOC contents were determined by ASTM D 2369-01. Exempt compounds were not considered.
- 3) Evaporation (weight loss) rates were calculated from weight and time measurements taken under ambient conditions using a thermogravimetric analyzer. Sample loading - 20 to 30 mg. Purge gas - clean, dry, compressed air @ 108 sccm.

**Technology Assessment to Determine the Relationship of Solvent Vapor
Pressure and Mass VOC Emissions**

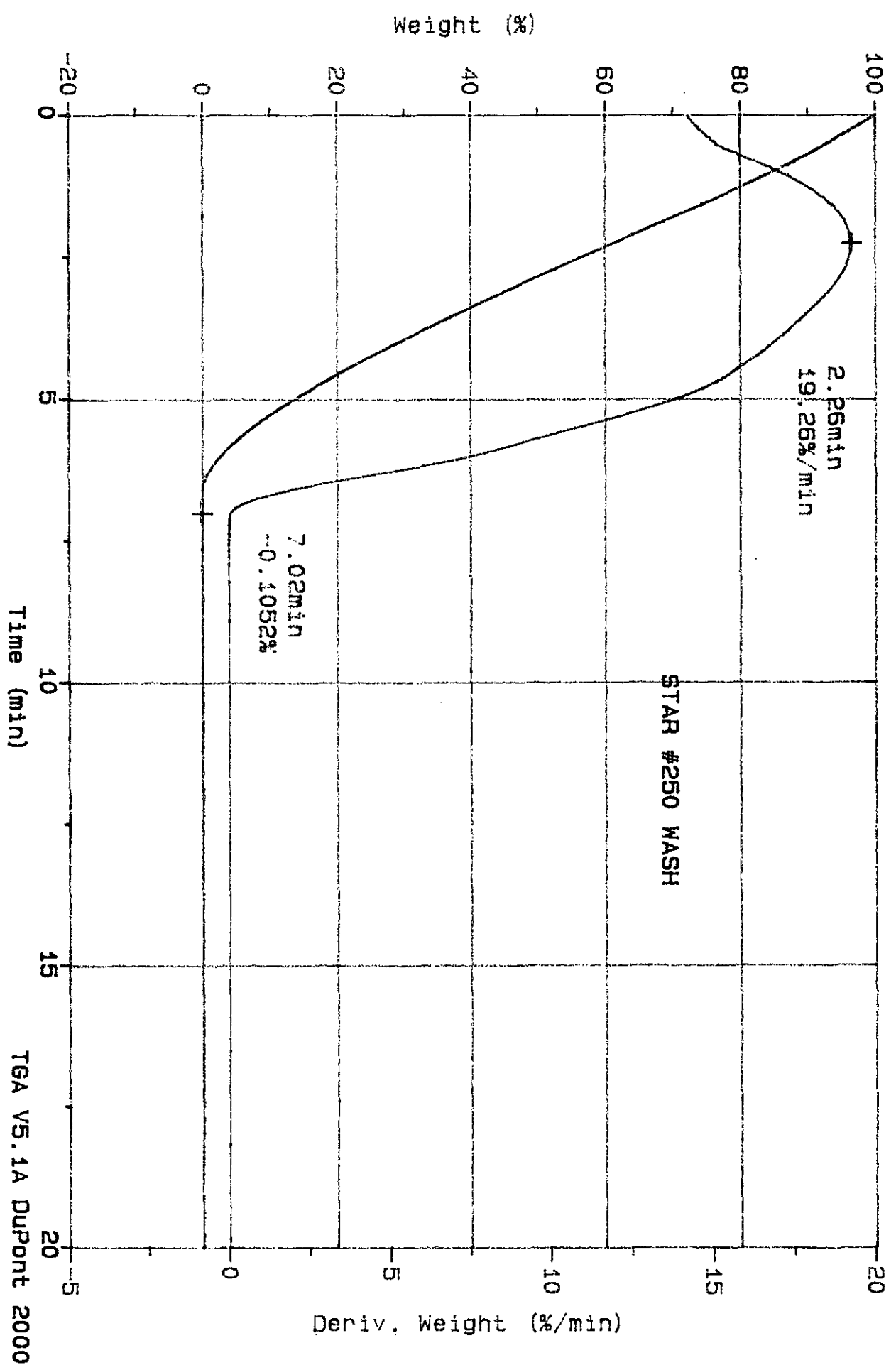
Attachment F

Recorded Evaporation Curves

Sample: STAR PRODUCTS #250 BLANKET WASH
Size: 22.0710 mg
Method: PRISCO 1HR
Comment: 01131-01-011

TGA

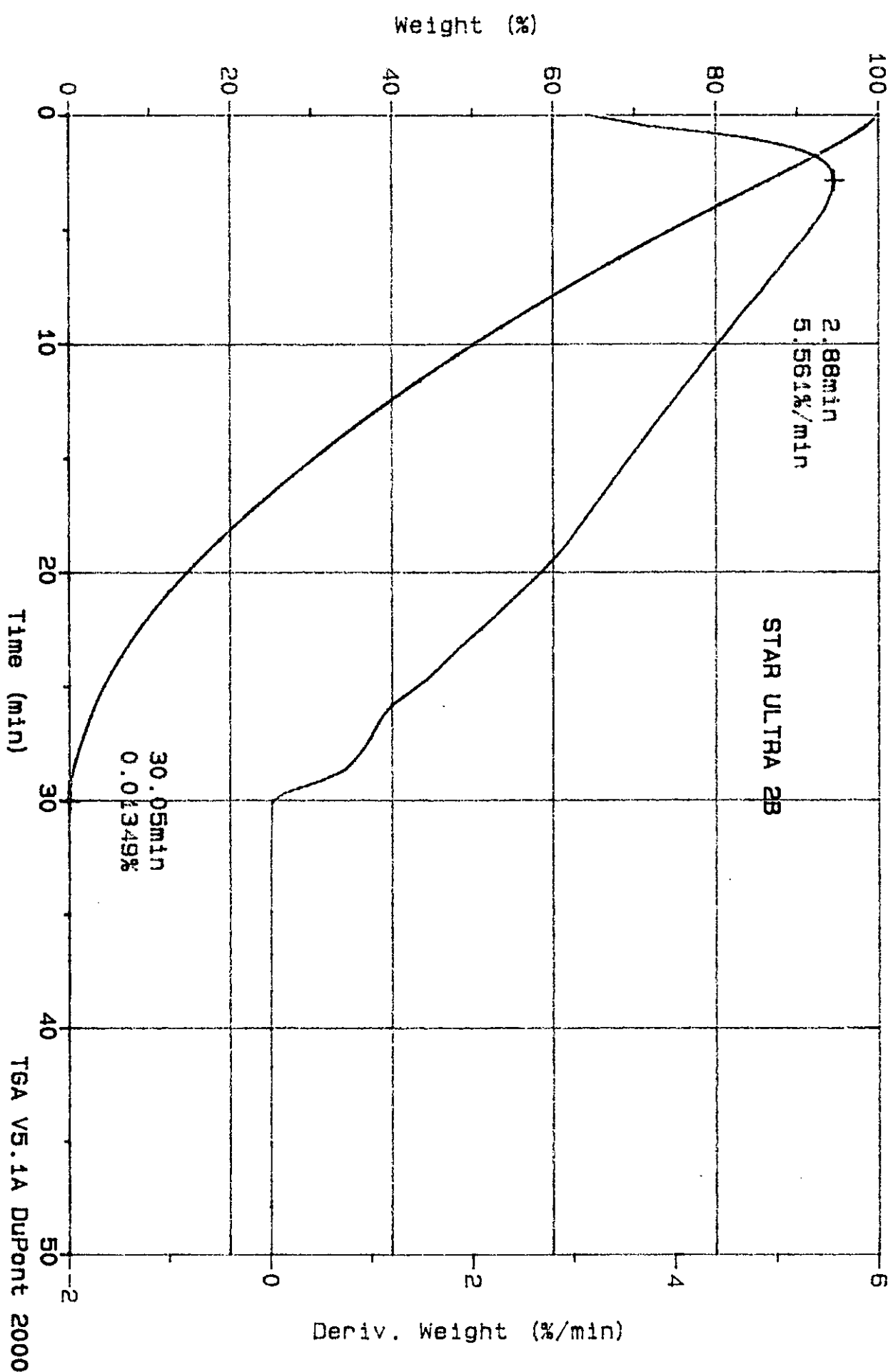
File: C:0113101.012
Operator: phil/SALLY
Run Date: 17-May-01 00:19



Sample: STAR PRODUCTS ULTRA 2B
Size: 24.3990 mg
Method: PRISCO 1HR
Comment: 01131-01-010

TGA

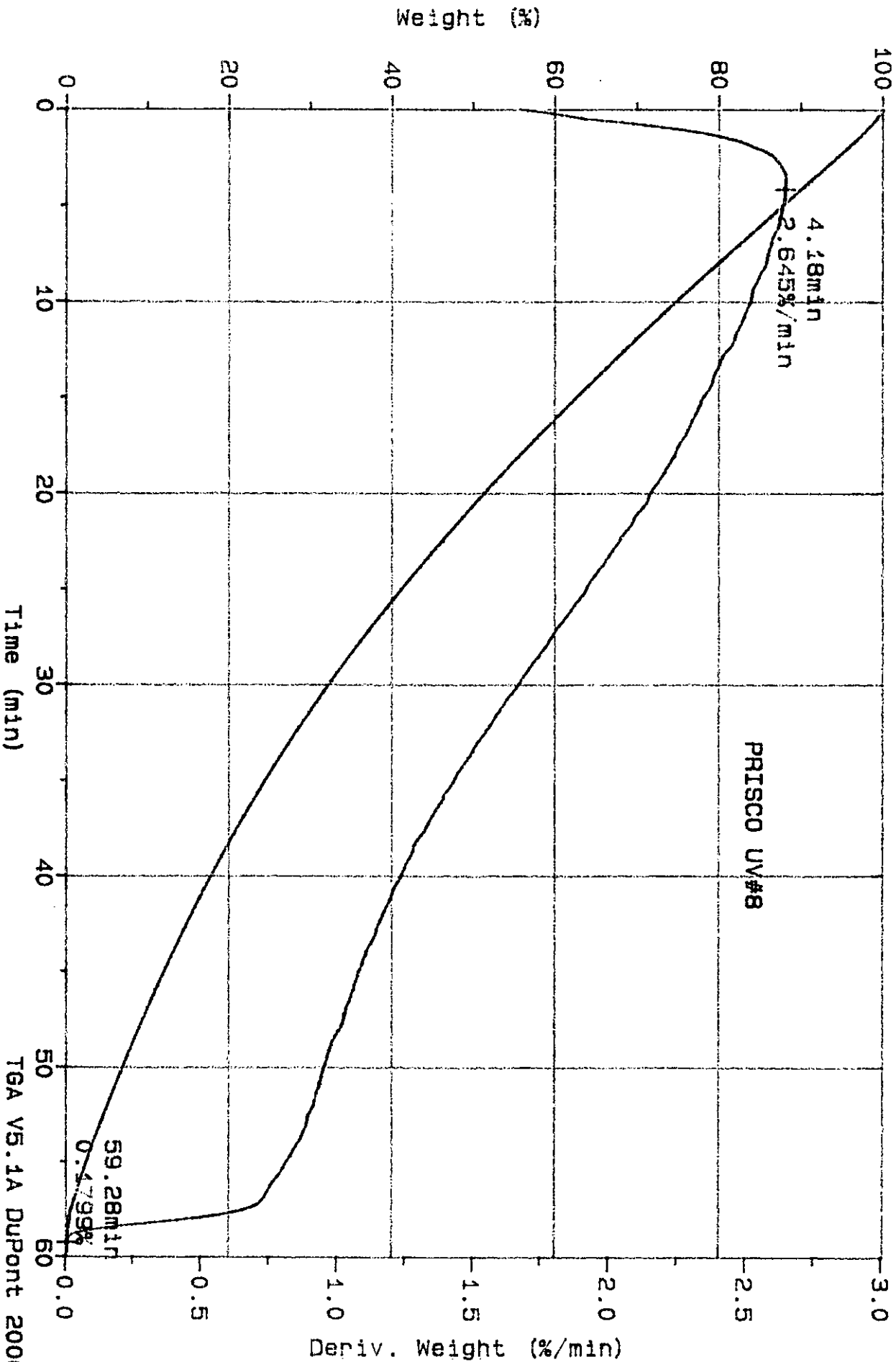
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Operator: phil/SALLY
Run Date: 16-May-01 22:12



Sample: PRISCO UV#8
Size: 27.6230 mg
Method: PRISCO 1HR
Comment: 01131-01-006

TGA

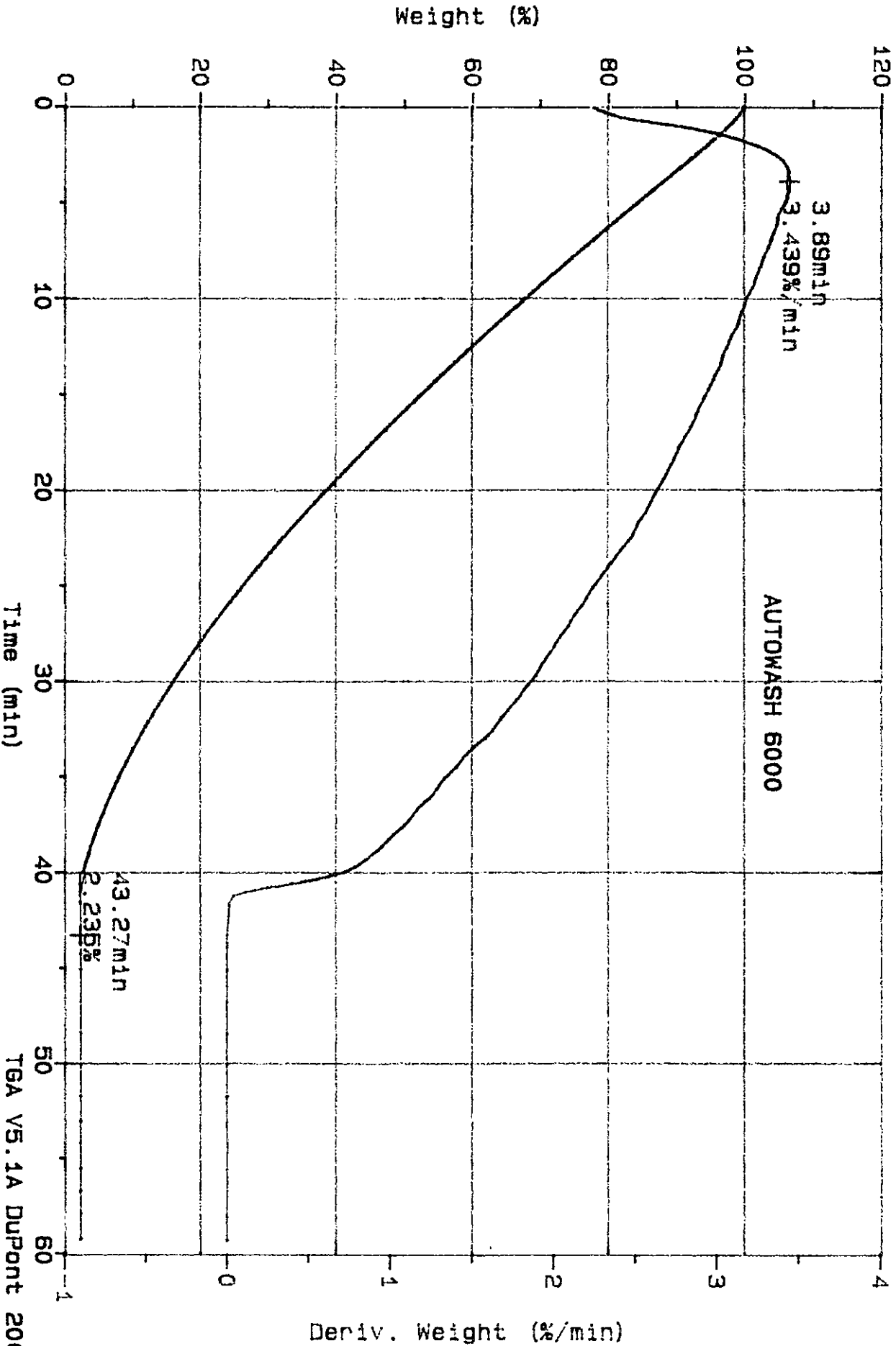
File: C:0113101.006
Operator: PH11/SALLY
Run Date: 14-May-01 21:34



Sample: PRISCO AUTOWASH 6000
Size: 22.5660 mg
Method: PRISCO 2HRS.
Comment: 01131-01-004

TGA

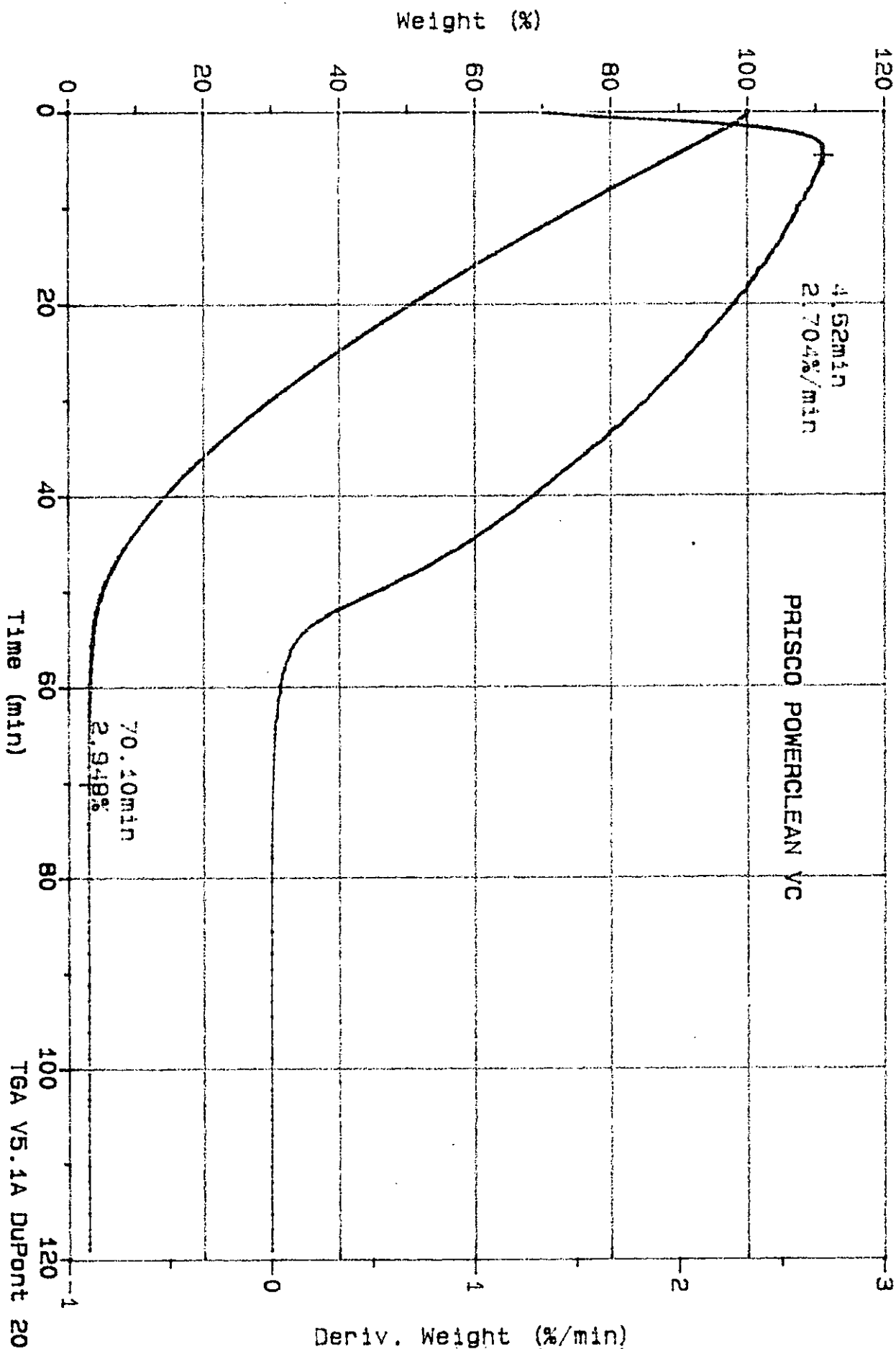
File: C:0113101.004
Operator: PHIL/SALLY
Run Date: 14-May-01 19:21



Sample: PRISCO (POWER CLEAN VC)
Size: 25.2190 mg
Method: PRISCO
Comment: 01131-01-003

TGA

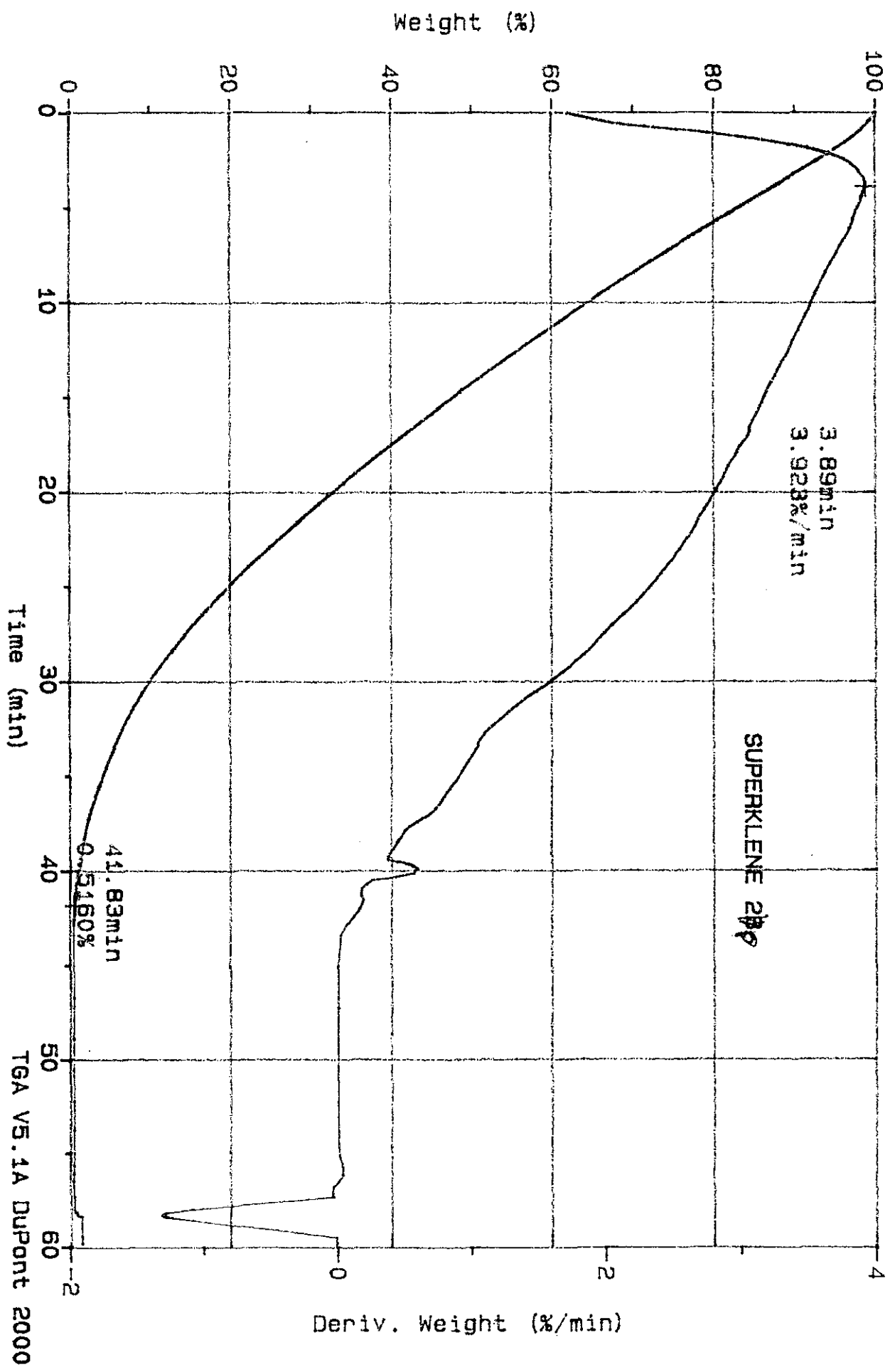
File: C:0113101.003
Operator: ph11/SALLY
Run Date: 10-May-01 23:19



Sample: PRISCO SUPERKLENE 2PP
Size: 23.0270 mg
Method: PRISCO 1HR
Comment: 04131-01-001

TGA

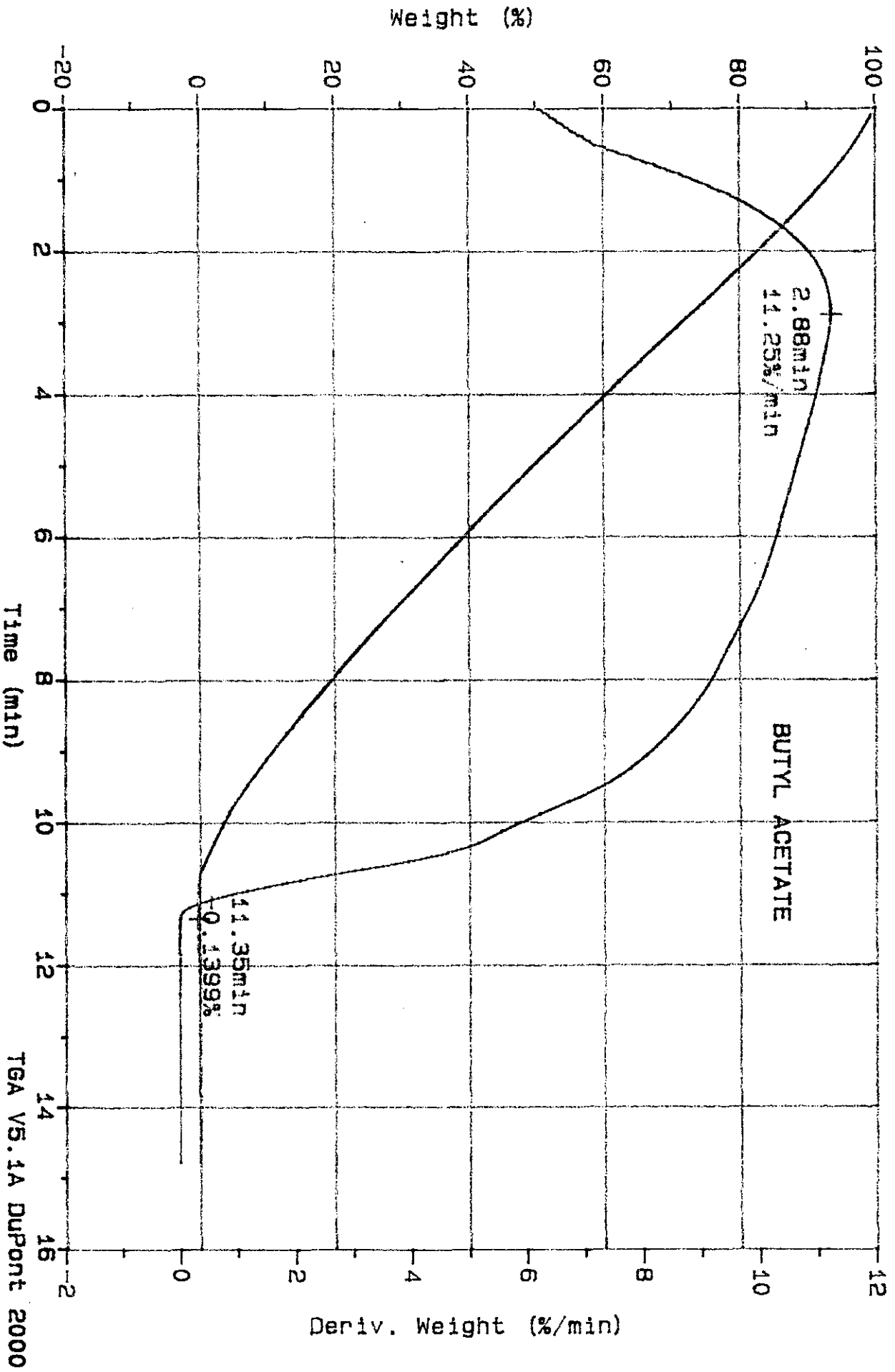
File: C:0413104.002
Operator: phil/SALLY
Run Date: 14-May-01 18:11



Sample: BUTYL ACETATE
Size: 24.8940 mg
Method: PRISCO 1HR

TGA

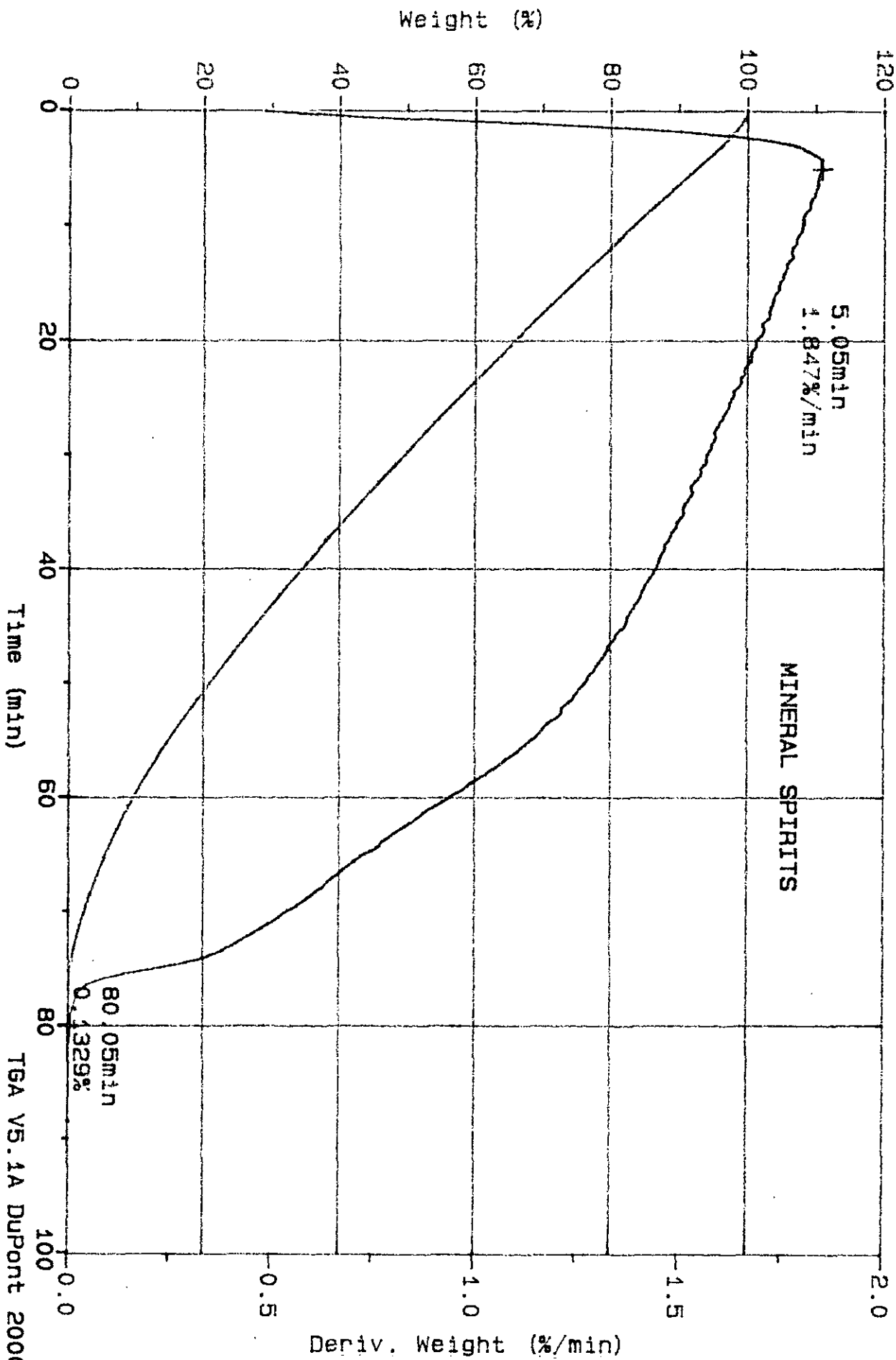
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Operator: phil/SALLY
Run Date: 22-May-01 00:32



Sample: MINERAL SPIRITS CAS 64742-48-9
Size: 25.7170 mg
Method: PRISCO 1HR
Comment: ISOPARAFIN ISOPAR K EXXON

TGA

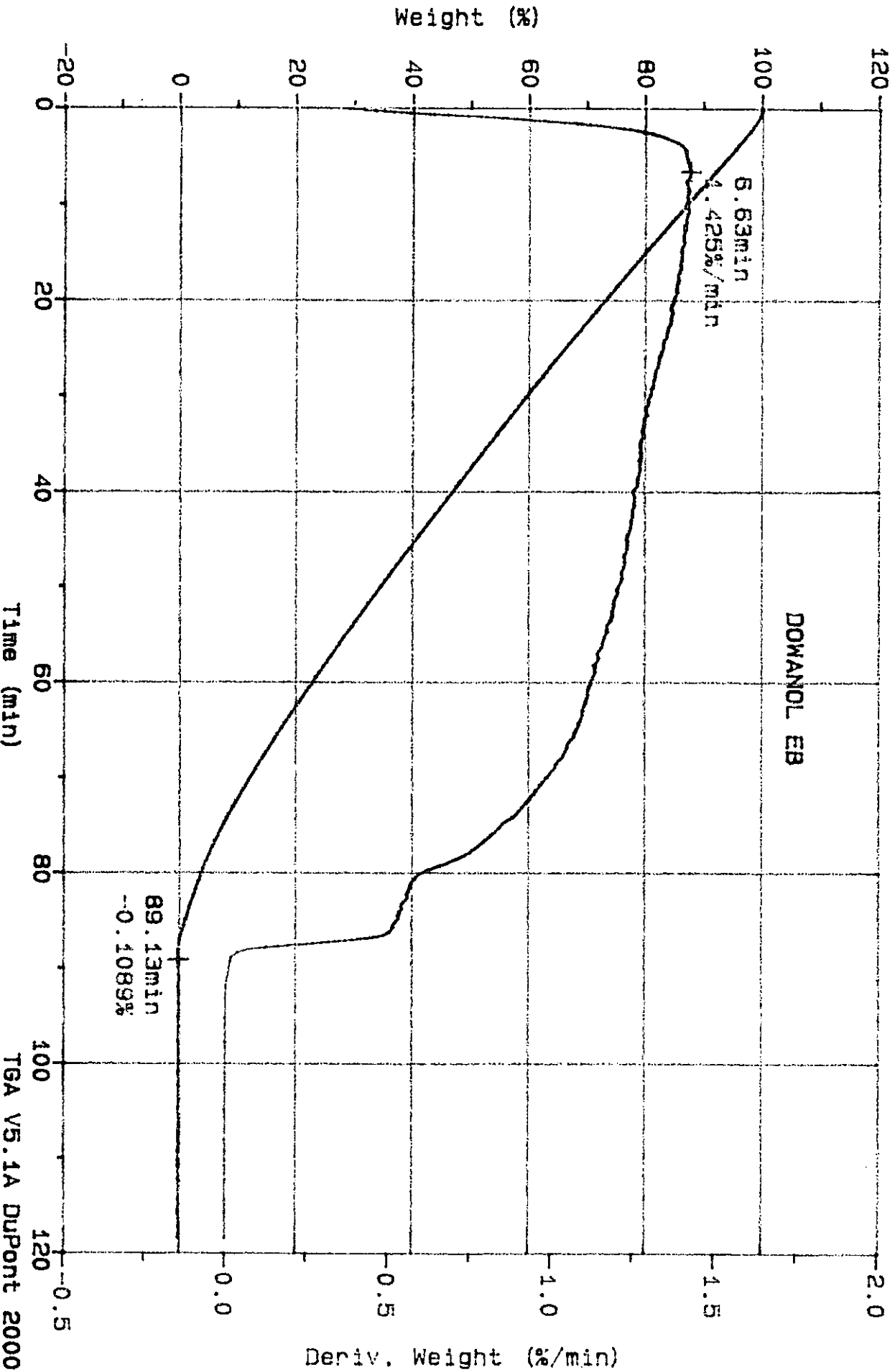
File: C:0113101.013
Operator: phil/SALLY
Run Date: 17-May-01 02:46



Sample: DOWANOL EB EGBE ALDRICH
Size: 27.2830 mg
Method: PRISCO 2HRS.
Comment: ETHYLENE GLYCOL BUTYL ETHER, LOT 01004KI

TGA

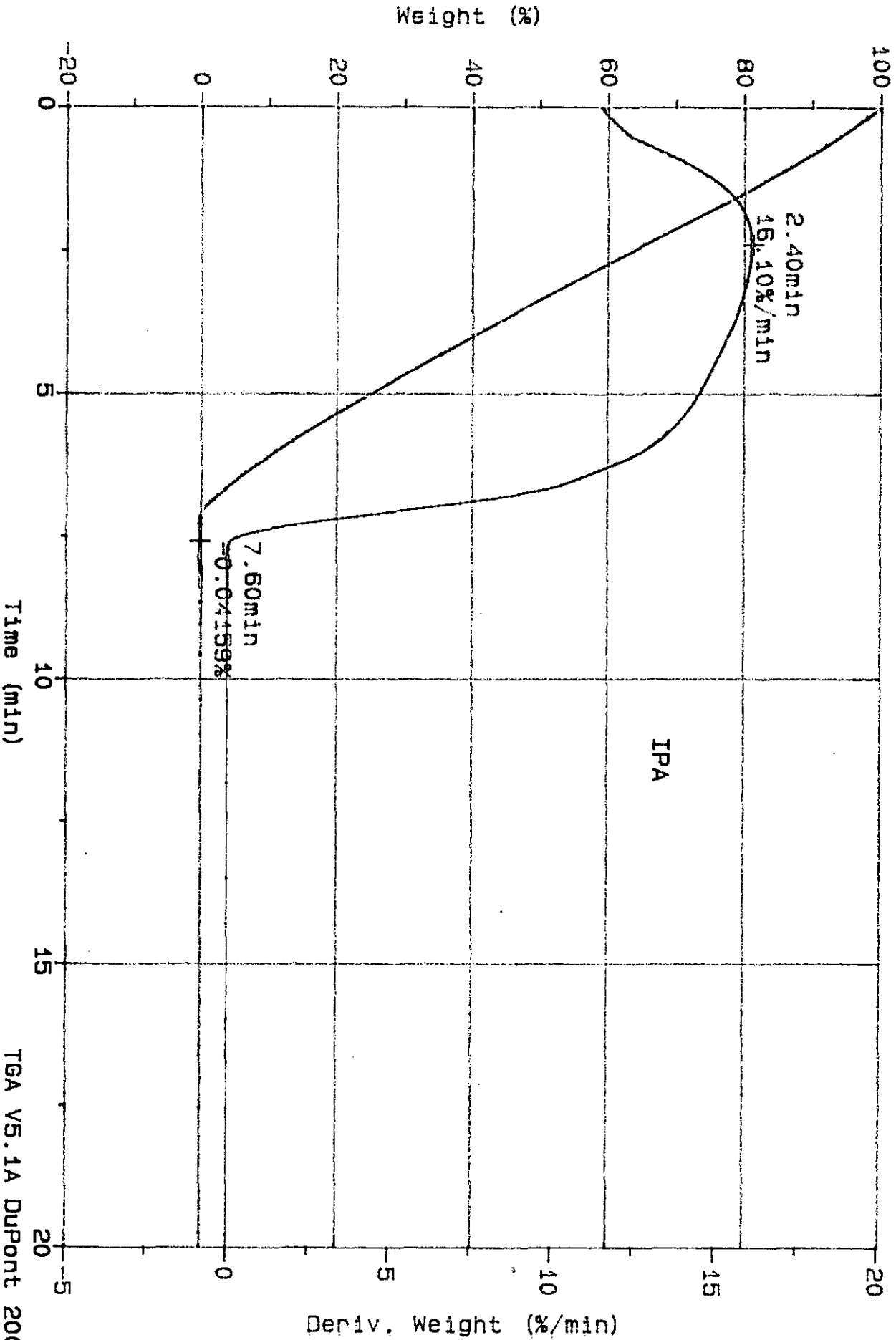
File: C:0113101.015
Operator: phil/SALLY
Run Date: 30-May-01 19:10



Sample: 2-PROPANOL BAKER LOT E50642
Size: 21.6390 mg
Method: PRISCO 1HR
Comment: IPA

TGA

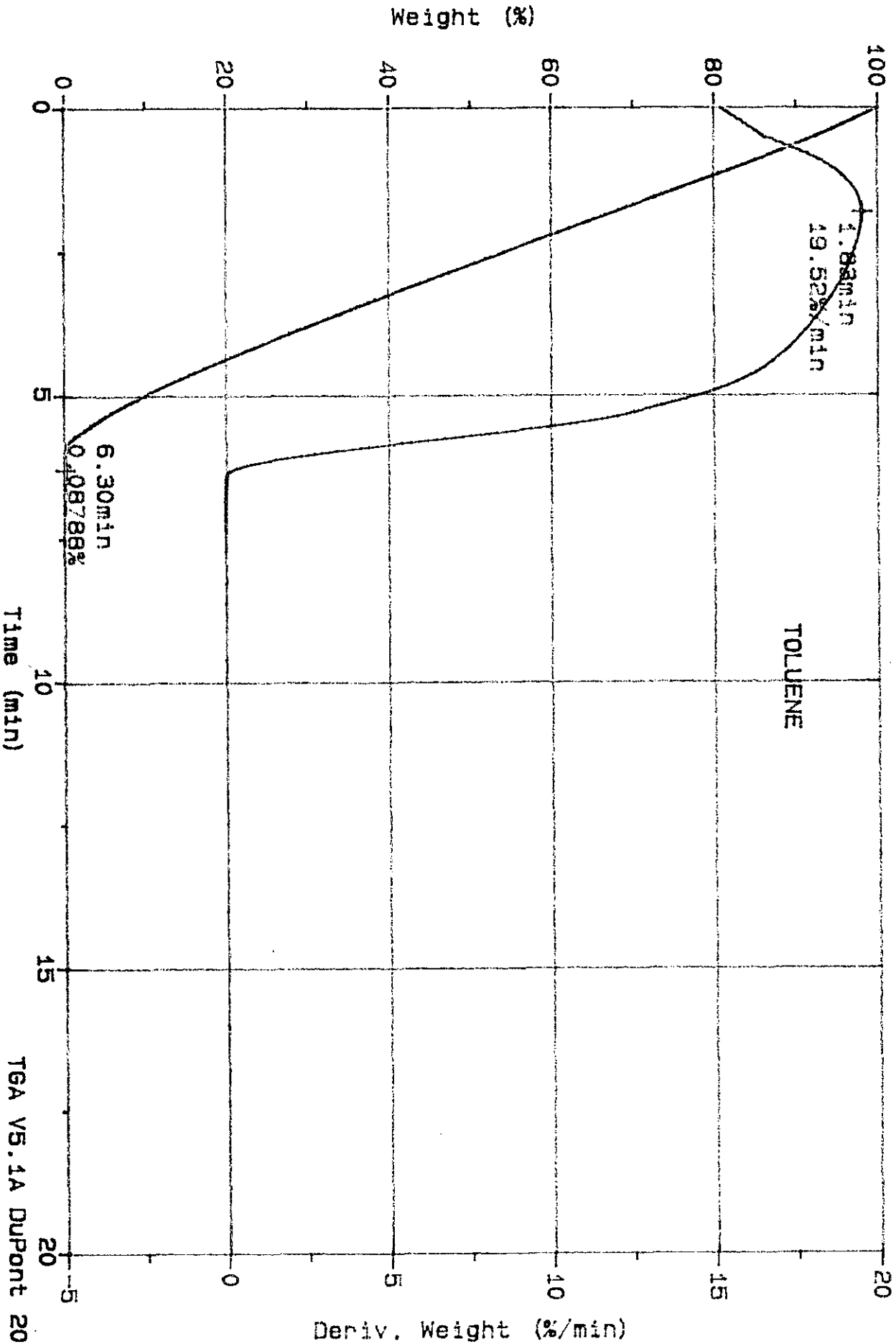
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Operator: PHIL/SALLY
Run Date: 31-May-01 20:28



Sample: TOLUENE BAKER LOT H03254
Size: 26.6280 mg
Method: PRISCO 1HR
Comment: TOLUENE

TGA

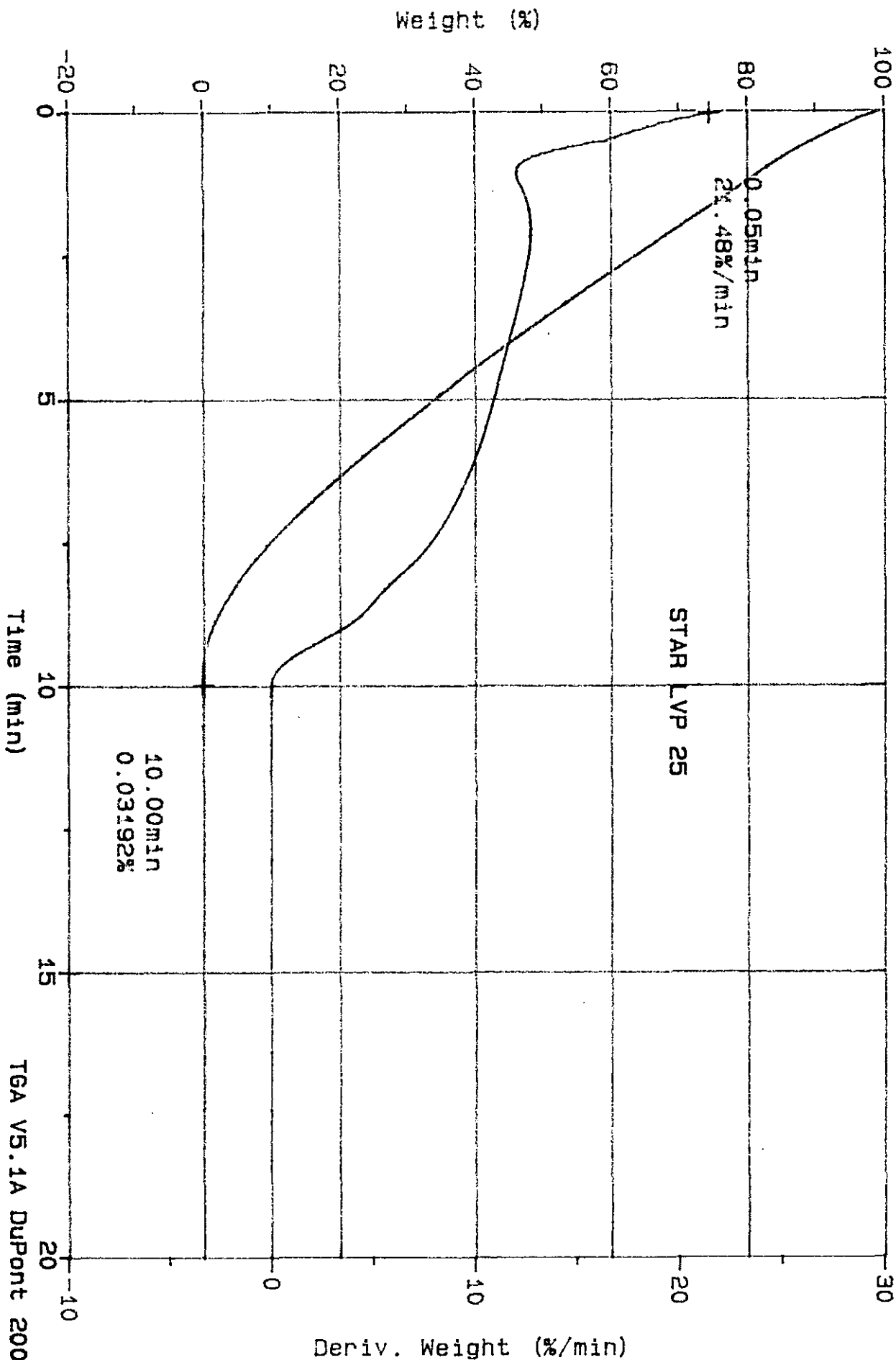
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Operator: phil/SALLY
Run Date: 31-May-01 21:20



Sample: STAR PRODUCTS LVP 25
Size: 20.5210 mg
Method: PRISCO 1HR
Comment: 01131-01-009

TGA

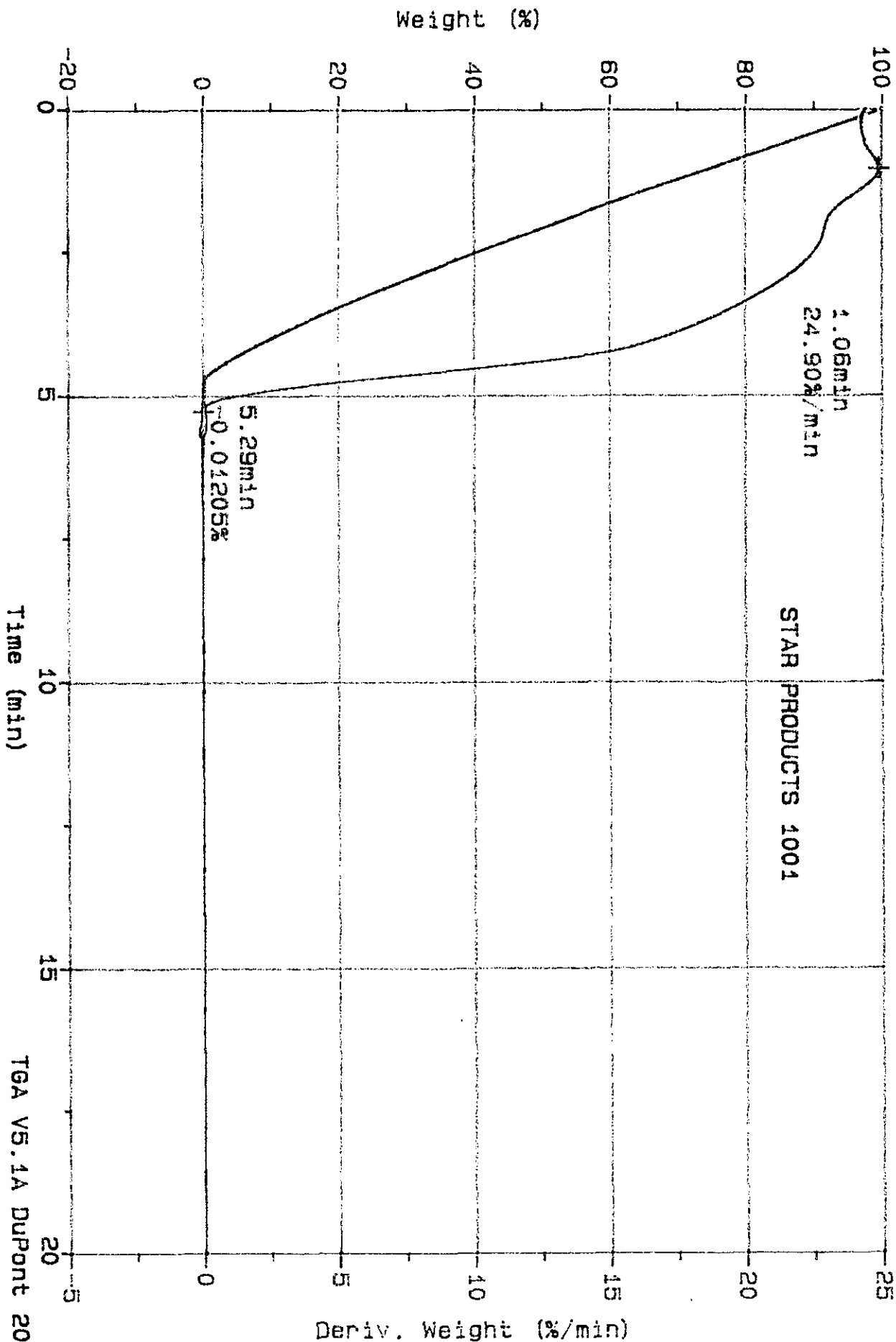
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Operator: phil/SALLY
Run Date: 16-May-01 21:03



Sample: STAR PRODUCTS 1001
Size: 20.0500 mg
Method: PRISCO 1HR
Comment: 01131-01-008

TGA

File: C:0113101.009
Operator: phil/SALLY
Run Date: 16-May-01 20:15



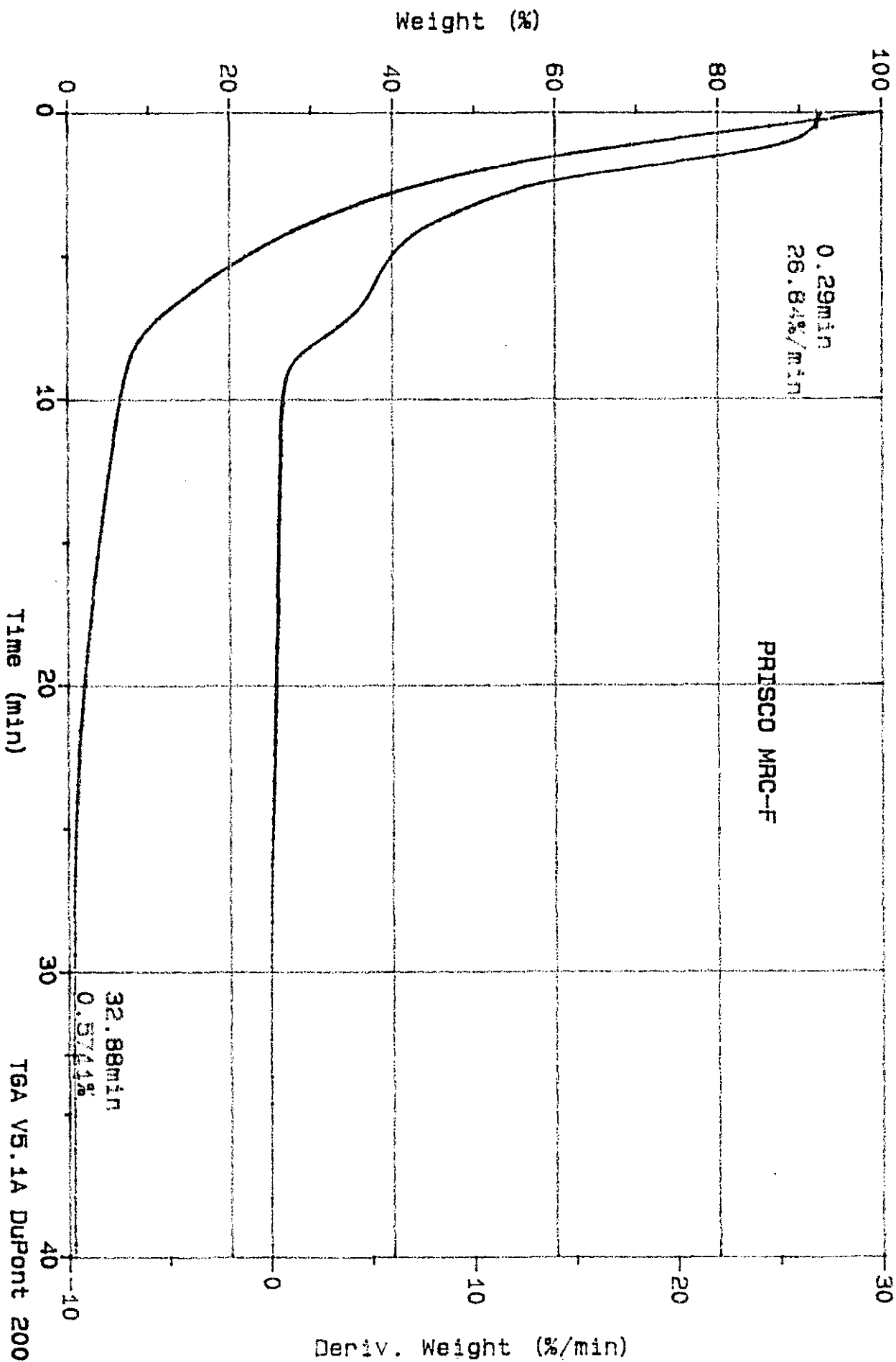
Time (min)

TGA V5.1A DuPont 2000

Sample: PRISCO (MRC-F)
Size: 20.1640 mg
Method: PRISCO 1HR
Comment: 01131-01-002

TGA

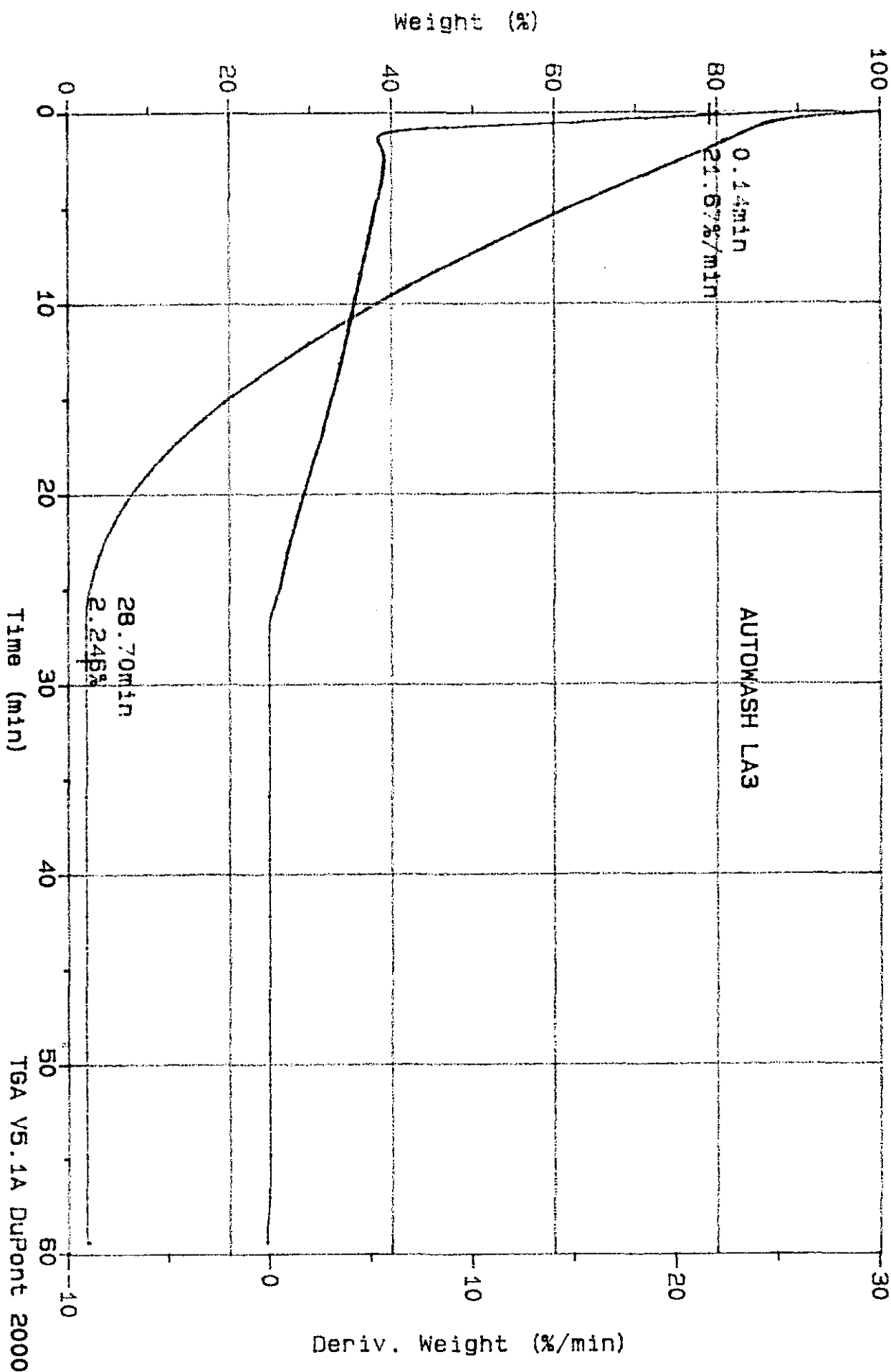
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Operator: ph11/SALLY
Run Date: 11-May-01 01:43



Sample: PRISCO AUTOWASH LA3
Size: 19.2750 mg
Method: PRISCO 1HR
Comment: 01131-01-005

TGA

File: C:0113101.005
Operator: phil/SALLY
Run Date: 14-May-01 20:28



Sample: PRISCO SUPERKLENE 11C
Size: 23.7060 mg
Method: PRISCO 3 HAS.
Comment: 01131-01-007

TGA

File: C:0113101.008
Operator: phil/SALLY
Run Date: 15-May-01 03:10

