California Environmental Protection Agency

Air Resources Board

Test Procedure for Leaks from Small Containers of Automotive Refrigerant

TP-503

Adoption Date: July 20, 2009
As Last Amended: January 5, 2010

NOTE: This document, approved by the Air Resources Board at its January 22, 2009 hearing for incorporation by reference in California Code of Regulations (CCR), title 17, sections 95360 through 95370, was originally shown without underline as permitted by California Code of Regulations, title 1, section 8. The modifications are indicated in underline to indicate additions and in ~~strikeout~~ to indicate deletions.

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The definitions in Section 95361 of Title 17, California Code of Regulations (CCR) apply to this test procedure.

In these procedures, the term "ARB" refers to the California Air Resources Board, and the term "Executive Officer" refers to the ARB Executive Officer or his or her authorized representative.

1. APPLICABILITY

This test procedure is used by manufacturers of small containers of automotive refrigerant and ARB to determine the leakage rate of small containers of automotive refrigerant that are subject to the requirements of Title 17,CCR section 95360 *et seq.* Specifically, this test procedure will specify the equipment, procedures, and calculations to determine if a small container of automotive refrigerant complies with the leakage rate specified in section 2.1(B) of the Certification Procedures for Small Containers of Automotive Refrigerant, adopted ~~[BARCU will insert]~~ July 20, 2009, and last amended on [INSERT DATE OF AMENDMENT],

Requirement to Comply with All Other Applicable Codes and Regulations

Approval of a small container of automotive refrigerant by the Executive Officer does not exempt the container from compliance or with other applicable codes and regulations such as local, State or federal safety codes and regulations.

Safety

This test procedure involves the use of materials under pressure, and operations and should only be used by or under the supervision of those familiar and experienced in the use of such materials and operations. Appropriate safety precautions should be observed at all times while performing this test procedure.

2. PRINCIPLE AND SUMMARY OF TEST PROCEDURE

This procedure is used to determine the leakage rate of small containers of automotive refrigerant (small cans). Testing will involve subjecting both full and partially empty cans in both upright and inverted positions at two temperatures: 73 ^{o}F and 130 ^{o}F.

Thirty cans are tested under each condition for a total of 240 cans tested. Cans are brought to temperature stability, weighed, then stored for 30 days under specified conditions of temperature, orientation, and state of fill, then re-weighed. Leakage rate (grams/year) is estimated by (weight loss in grams) *365 / (days duration). The leakage rate is then compared to a standard of 3 grams/year to determine if a given small can complies with the leakage rate specified in section 2.1(B) of the Certification Procedures for Small Containers of Automotive Refrigerant, adopted ~~[BARCU will insert]~~ July 20, 2009, and last amended on [INSERT DATE OF AMENDMENT], .

3. BIASES AND INTERFERENCES

3.1. Contaminants on the operator's hands can affect the weight of the can and the ability of the can to absorb moisture. To avoid contamination of the can, the balance operator should wear gloves while handling the small cans.

3.2. Weight determinations can be interfered with by moisture condensing on the can and by thermal currents generated by temperature differences between the can and the room temperature. The small cans cool during discharge and could cause condensation. For these reasons, cans must be equilibrated to balance room temperature for at least four hours before weighing.

3.3. Variations in the temperature, pressure, and humidity of the ambient air will cause variations in the buoyancy of the small can. These variations should typically be less than 25 mg for a small can. If the can is not leaking at all, then the uncorrected weight changes will be within the range of 0 +/- 25 mg, which is about ten percent of the 247 mg loss expected after thirty days for a can leaking at 3 g/yr. In that case buoyancy corrections can be omitted. If the absolute value of the uncorrected weight change exceeds 25 mg, then all calculations must be made using weights corrected for buoyancy based on the temperature, pressure, and humidity of the weighing room.

3.4. Some electronic balances are sensitive to the effects of small static charges. The small can should be placed directly on the balance pan, ensuring metal to metal contact. If the balance pan is not grounded, the can and balance pan should be statically discharged before weighing.

4. SENSITIVITY AND RANGE

The mass of a full can could range from roughly 50 to 1000 grams depending on the container capacity. A top loading balance, capable of a maximum weight measurement of not less than 1,000 grams and having a minimum readability of 0.001 gram, reproducibility and linearity of ± 0.002 grams, must be used to perform mass measurements (examples: Sartorius LA1200S, Mettler XS1003S, etc).

5. EQUIPMENT

5.1. A top loading balance that meets the requirements of Section 4 above.

5.2. A NIST traceable working standard mass for balance calibration. A NIST traceable working standard mass for a balance linearity check. A reference mass to serve as a "blank" can.

5.3. A enclosure capable of controlling the internal air temperature from 73 $^{\circ}$F +/- 5 $^{\circ}$F and an enclosure capable of controlling the internal air temperature to 130 $^{\circ}$F, +/- 5 $^{\circ}$F.

5.4. A temperature instrument capable of measuring the internal temperature of the temperature conditioning enclosures and the balance room with a sensitivity of +/- 2 $^{\circ}$F.

5.5. A barometric pressure instrument capable of measuring atmospheric pressure at the location of the balance to within +/- 0.02 inches of mercury.

5.6. A relative humidity measuring instrument capable of measuring the relative humidity (RH) at the location of the balance with a sensitivity of +/-2% RH.

5.7. A hose with appropriate fitting for dispensing refrigerant from the small can to a recovery machine.

5.8. A refrigerant recovery machine to collect the discharged refrigerant from cans being tested.

6. CALIBRATION PROCEDURES

Calibrations are applied to the balance and to the support equipment such as temperature, humidity, and pressure monitoring equipment. Procedures for calibration are not spelled out here. General calibration principals for the support equipment and the balance are described in Section 11, Quality Assurance / Quality Control. Detailed calibration procedures for measurement made using the balance are contained in Balance Protocol (BP–A1) "Balance Protocol for Gravimetric Determination of Sample Weights using a Precision Balance" adopted ~~[BARCU will insert]~~ July 20, 2009, and last amended on [INSERT DATE OF AMENDMENT], which is incorporated by reference herein.

7. CAN PREPARATION

7.1. Receive a batch of 240 cans of one design to be tested. These may include several SKUs from different manufacturers if the container and valve combination are the same.

7.2. Clean cans with Alkanox solution or equivalent and dry with lint free towel.

7.3. Confirm that the sample ID sticker on the can matches the sample ID on the chain of custody forms.

7.4. Select a reference mass similar to the weight of a full can. If multiple sets of similar sized cans are being tested, only one reference mass is needed; it can be used with all sets. Store the reference mass in the balance area.

7.5. Discharge the contents of one half of the cans (120 cans) into the refrigerant recovery machine using normal DIY dispensing procedures until each small can is approximately half full.

7.6. Select a reference mass similar the weight the half full small can. If multiple sets of similar size cans are being tested, only one reference mass is needed; it can be used with all sets. Store the reference mass in the balance area.

8. CAN WEIGHING

Weighing cans on the balance is done in accordance with Balance Protocol (BP-A1) adopted ~~[BARCU will insert]~~ <u>July 20, 2009 and last amended on [INSERT DATE OF AMENDMENT]</u>, which is incorporated by reference herein. The Balance Protocol describes how to conduct weight determinations including appropriate calibration and QC data. This section, Can Weighing, describes the overall process, not the details of how to use the balance.

Initial Weights

8.1. Put on gloves. Check the cans for contamination.

8.2. Place the 240 cans into a location where they can equilibrate to balance room temperature. Record the can test IDs and the equilibration start time on the Small Can Test Data Forms (Form TP–503–01) in sets of thirty, one form for each of the eight each test conditions.

8.3. Let cans equilibrate for at least four hours.

8.4. Weigh the set of 240 cans and the reference weights using the Balance Protocol (BP–A1) “Balance Protocol for Gravimetric Determination of Sample Weights using a Precision Balance” adopted ~~[BARCU will insert]~~ <u>July 20, 2009 and last amended on [INSERT DATE OF AMENDMENT]</u>, which is incorporated by reference herein, and log the results to the

Balance Weighing Log Form (Form TP–503–02) attached to this test procedure.

8.5. Transfer data from the Balance Weighing Log Form to the Small Can Test Data Forms in sets of 30, one set for each of the eight conditions to be tested.

Thirty-Day Soak

8.6. Place each set of 30 cans into the appropriate orientation and temperature for soaking:

30 full cans – 73 °F, upright

30 full cans – 73 °F, inverted

30 full cans – 130 °F, upright

30 full cans – 130 °F, inverted

30 half-full cans – 73 °F, upright

30 half-full cans – 73 °F, inverted

30 half-full cans – 130 °F, upright

30 half-full cans – 130 °F, inverted

8.7. Soak the cans for 30 days undisturbed.

Final Weighing

8.8. Place the 240 cans into a location where they can equilibrate to balance room temperature.

8.9. Let the cans equilibrate for at least four hours.

8.10. Weigh the set of 240 cans, the reference weights, and any additional sets of cans using the Balance Protocol (BP–A1) “Balance Protocol for Gravimetric Determination of Sample Weights using a Precision Balance” adopted ~~[BARCU will insert]~~ July 20, 2009 and last amended on [INSERT DATE OF AMENDMENT], which is incorporated by reference herein.

8.11. Transfer data from the Balance Weighing Log Form to the corresponding Small Can Test Data Forms.

Can Storage (only applicable to ARB)

8.12. If the cans can pass the leak rate criteria, the cans may be recycled. (Return the cans to the place of purchase for recycling).

8.13. If the cans do not pass the leak rate criteria, then mark the set with the message “Hold until released by Enforcement Division”. Transfer the entire set of cans to safe storage location.

9. CALCULATIONS

Corrections for Buoyancy

The calculations in this section are described in terms of “weight.” Mass is a property of the can, whereas weight is a force due to the effects of buoyancy and gravity. Procedures for correcting the effect of buoyancy are given in Attachment A of this procedure. Ignoring buoyancy, i.e. using weight data uncorrected for buoyancy effects, is acceptable for a thirty day test if the absolute magnitude of the weight change is less than 25 mg. If the uncorrected weight change exceeds 25 mg for any can, then correct all can weights for buoyancy using the procedures in Attachment A before performing the calculations described below.

Calculation of Leak Rate

The emission rate in grams/day for each can is calculated by subtracting the final weight from the initial weight and then dividing the weight difference by the time difference measured in days to the nearest hour (nearest 1/24 of a day). The emission rate in g/day is multiplied by 365 to determine emission rate in grams/yr. If the annual emission rate for any can exceeds the entire can contents, then the annual emission rate for that can is adjusted to equal the entire can contents/year (e.g., about 350 g/yr for a 12 ounce can). The annual emission rate for the purpose of the test is calculated by averaging the 240 individual adjusted annual emission rates and rounding to 2 decimal places. The cans fail the test if the adjusted annual emission rate averaged over 240 cans is greater than 3.00 grams/yr. The calculations are described below.

Loss rate for each can

$E i_{daily} = (W i_{final} - W i_{initial}) / (D i_{final} - D i_{initial})$, grams/day
$E i_{annual} = 365 * E i_{dailly}$ grams/year
$E I_{adjusted} = \text{Minimum of } (E i_{adjusted}, C i/\text{year})$ grams/yr

Where,

$E i$ = emission rate
$W i_{final}$ = weight of can *i* after soaking (grams)
$W i_{initial}$ = weight of can I before soaking (grams)
$D i_{final}$ = date/time of final weight measurements (days)
$D i_{initial}$ = date/time of initial weight measurements (days)
$C i$ = original factory mass of refrigerant in can *i*

Note Date/Times are measured in days. Microsoft Excel stores dates and times in days, and the calculations can be made directly in Excel. If calculations are made manually, calculate serial days to the nearest hour for each date and time as follows:

$D = \text{Julday} + \text{Hour}/24$

Where,

Julday = serial day of the year: Jan 1 = 1, Jan 31 = 31, Feb 1 = 32, etc.
Hour = hour of day using 24-hour clock, 0 to 23

Calculate the average loss rate for the 240 cans as follows:

$$E_{mean} = [\text{Sum}(E_{adjusted}\,i),\ i=1 \text{ to } 240\ ] /240$$

10. RECORDING AND REPORTING DATA

During can weighing, record the can weights and date/times on the Balance Weighing Log Form. After each weighing session, transfer the measured weights and date/times from the Balance Weighing Log Form to the Small Can Test Data Form.

At the end of the test, complete the calculations described in Section 9, Calculations, and record the results on the Small Can Test Data Forms.

At the end of the test, transmit a copy of the Small Can Test Data Forms to the Project Engineer.

11. QUALITY ASSURANCE / QUALITY CONTROL

11.1. All temperature, pressure, and humidity instruments should be calibrated at least annually against NIST traceable laboratory standards. The main purpose of the NIST traceable calibration is to establish the absolute accuracy of the device. The instruments should also be checked periodically such as weekly, monthly, or quarterly against intermediate standards or against independent instruments. For example, a thermocouple can be checked weekly against a wall thermometer. A barometer or pressure gauge can be checked weekly by adjusting to sea level and comparing with local airport data. The main purpose of the frequent checks is to verify that the device has not failed in some way. This is especially important for electronic devices such as a digital thermometer, but even a liquid filled thermometer can develop a problem such as a bubble.

11.2. The balance should be serviced and calibrated at least annually by an independent balance service company or agency using NIST traceable reference masses. Servicing verifies accuracy and linearity, and the maintenance performed helps ensure that a malfunction does not develop.

11.3. The balance must also be calibrated and its linearity checked with working standards before and after each weighing session, or before and after each group of 24 cans if more than 24 cans are weighed in a session. Procedures for calibrating and using the balance, as well as recording balance data, are described in the accompanying balance weighing protocol. These procedures include zero checks, calibration checks, and reference mass checks. Procedures for calculating quality control data from those checks are described in the balance protocol.

11.4. The small containers are cleaned then handled using gloves to prevent contamination. All equilibration and soaking must be done in a dust free area.

Form TP–503–01: Small Can Test Data Form

Enforcement Lot ID ____________________

Full: ☐ Half full: ☐

Upright: ☐ Inverted: ☐

T=73 F: ☐ T= 130 F: ☐

Can ID	Date: ________ Initial time (hour)	Initial weight (g)	Date: ________ Final Time (hour)	Final Weight (g)	Delta Days	Delta Weight (g)	Adjusted Annual Rate (g/yr)
________	________	________	________	________	________	________	________
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Number of Samples: ____________

Technician: ____________

Average Loss Rate: ____________

Standard Deviation: ____________

Comments: ____

Form TP–503–02: Balance Data Log Form

						QC	Can	Can	Recorded	
Rec #	Date	Time	Proj.	Prot.	Tech.	Code	Type	ID#	grams	Comment
1										
2										
3										
4										
5										
6										
7										
8										
9										
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Attachment A

Compensation of Weight Data for Buoyancy and Gravity Effects

Gravity

Variations in gravity are important only when weighing objects under different gravitational fields, i.e. at different locations or at different heights. Since the balance procedures calibrate the balance against a known mass (the calibration "weight") at the same location where sample objects are weighed, there is no need to correct for location. Although both the sample and the calibration weight are used at the same location, there will be a difference in the height of the center of gravity of the sample object (small can) and the center of gravity of the reference mass (calibration weight). However, this difference in height is maintained during both the initial weights and final weights, affecting the initial and final weights by the same amount, and affecting the scale of the weight difference by only a few ppm. In any event, the magnitude of this correction is on the order of 0.3 ug per kg per mm of height difference. A difference on the order of 100 mm would thus yield a weight difference of about 0.03 mg, which is insignificant compared to our balance resolution which is 0.001 g or 1 mg.

Based on the discussion above, no corrections for gravity are necessary when determining weight changes in small cans.

Buoyancy

Within a weighing session, the difference in density between the sample object and the calibration weight will cause the sample object weight value to differ from its mass value due to buoyancy. For a 1-liter object in air at 20^{o}C and at 1 atm, the buoyant force is about 1.2 grams. The volume of a 1 kg object with a density of 8 g/cm3 (e.g. a calibration weight), is about 0.125 liters, and the buoyancy force is about 0.15 g. Variations in air density will affect both of these values in proportion. The net value being affected by variations in air density is thus on the order of 1.2 - 0.15 = 1.05 g. Air density can vary up or down by 2% or more due to variations in barometric pressure, temperature, and humidity. The buoyancy force will then vary up or down by 0.02 g, or 20 mg. This is significant compared to the weight change expected after one week for a can leaking at 3 grams per year, which is 57 mg.

Based on the discussion above, buoyancy corrections must be made.

Variables measured or calculated:

V_{can} = volume of can (cm^3). Estimate to within 10% by measuring the can dimensions or by water displacement. Error in the can volume will cause an error in the absolute amount of the buoyancy force, but will have only a small effect on the change in buoyancy force from day to day.

W_{can} = nominal weight of a can (g), used to calculate the nominal density of the can

ρ_{can} = nominal density of a small can (g/cm^3). The nominal values can be applied to corrections for all cans. It is not necessary to calculate a more exact density for each can. Calculate once for a full can and once for a half full can as follows:

$$\rho_{can} = W_{can} / V_{can}$$

T = Temperature in balance chamber (degrees Celsius)

RH = Relative humidity in balance chamber (expressed a number between 0 and 100)

P_{baro}= Barometric pressure in balance chamber (millibar). Use actual pressure, NOT pressure adjusted to sea level.

ρ_{air} = density of air in the balance chamber (g/cm^3). Calculate using the following approximation

$$\rho_{air} = \underline{0.001*}[0.348444*P_{baro} – (RH / 100)*(0.252*T – 2.0582)] / (T + 273.15)$$

ρ_{ref} = the reference density of the calibration weight (g/cm$_3^3$). Should be 8.0 g/cm^3.

Equation to correct for buoyancy

$$W_{corrected} = W_{reading} * (1 - \rho_{air} / \rho_{ref}) / (1 - \rho_{air} / \rho_{can})$$