Quantitative Evaluation of Chilling Effect of Aerosol Sprays

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Abstract ☐ A quantitative method was developed for comparative evaluation of chilling effect of aerosol sprays. Cooling curves were obtained by exposing a specified thermistor probe to the aerosol spray using the test chamber described. The drop in the temperature of the probe as a function of exposure time followed first-order kinetics. The chill index which represents the instantaneous cooling rate of the probe at 37.5° was used to compare the chilling effect of some common aerosol propellant mixtures with additives.

Keyphrases ☐ Aerosol sprays—chilling effect ☐ Apparatus—aerosol chill-effect determination ☐ Chill index—aerosol sprays ☐ Propellants, aerosol—chill-index effect

Chilling is a common effect observed with aerosol sprays resulting from the extremely rapid evaporation of liquid propellant and the expansion of the propellant vapor. Chilling effect of an aerosol spray is governed by the composition of the spray, spray rate, and spray pattern. Consequently, the extent of chilling varies over a wide range from one aerosol formulation to another and in many cases poses practical problems with respect to acceptability or efficacy of pharmaceutical and cosmetic aerosol products. While chilling is highly undesirable in the case of cosmetic products, such as deodorants and colognes and in pharmaceutical aerosols, such as nasal and inhalation sprays, a very high rate of chilling is essential for the efficacy of products such as anesthetic skin-refrigerant sprays used for minor surgical procedures. Hence, a quantitative method for comparison of chilling effects of aerosol sprays can be of considerable use in the formulation and/or evaluation of aerosol products.

Current methods of measurement of aerosol chill reported in the literature are based on the measurement of the temperature drop of a thermocouple sensor after exposure to the aerosol spray for a specified time interval at a specified distance from the actuator (1, 2). These methods have certain disadvantages that are likely to result in misleading conclusions in comparative evaluation of aerosol sprays. Particular mention must be made that the cooling of the sensor probe as a function of exposure time to the spray shows an exponential relationship. The temperature drop of the sensor probe is very rapid initially and diminishes continuously until an equilibrium temperature is reached. If the exposure time specified in the test procedure is relatively short, the temperature drop observed after the specified exposure time may not be the maximum temperature drop produced when the sensor probe is exposed to the given aerosol spray. Furthermore two sprays showing identical maximum temperature drop of the sensor probe may have quite different chilling effects if the equilibrium probe temperature is achieved much faster in one case as compared to the other.

The method described herein is based on the calculation of the instantaneous cooling rate of a specified thermistor probe exposed to the spray in the test chamber described. This instantaneous rate of cooling is dependent on both the maximum temperature drop of the probe and rate with which the equilibrium temperature of the probe is approached.

EXPERIMENTAL

Instrumentation—Figure 1 illustrates the instrumentation employed. The test chamber consisted of a rectangular, metal clad, wooden box 15.2 × 15.2 × 25.4 cm. (6 × 6 × 10 in.). The front wall of the chamber had a 2.54-cm. (1-in.) diameter opening. The thermistor probe[1] was positioned inside the chamber exactly facing the center of the opening 2.54 cm. (1 in.) away from the wall. The aerosol container to be tested was positioned in such a way that, upon actuation, the probe was exposed to the spray from a distance of 7.62 cm. (3 in.). The thermistor probe was connected to a telethermometer[2] whose output was recorded on a strip-chart recorder.[3]

Sample Preparation—For the evaluation of chilling effect of propellants and the effect of addition of additives such as ethanol, isopropanol, and acetone on the chilling effect of propellants, a standardized aerosol sample was used. Standardization was achieved by using the indicated components for each aerosol container.[4]

Weight of Fill—A uniform fill of 120 g. was employed. Commercial samples were tested exactly as purchased.

Operation—Cooling curves were obtained by exposing the probe to the spray continuously until the temperature reached a minimum value (T_m).

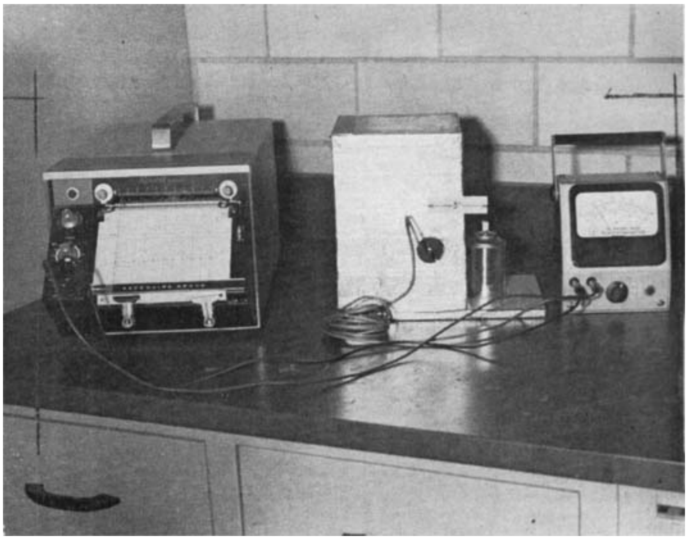

Figure 1—*Apparatus for the evaluation of chilling effect of aerosol sprays.*

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[1] Fisher 15-176-28.

[2] Fisher YS-1, model 425F.

[3] Esterline-Angus, 100 mv., multirange, variable speed, fast response.

[4] Container, Continental 202 × 204 can with 298 solder; valve, Risdon No. 6422, with epon-coated aluminum cup, neoprene gaskets; actuator, Aerosol Research No. RKN-62, 2-piece mechanical break-up, with 929 black plastic insert, 0.0201-1 in. orifice.

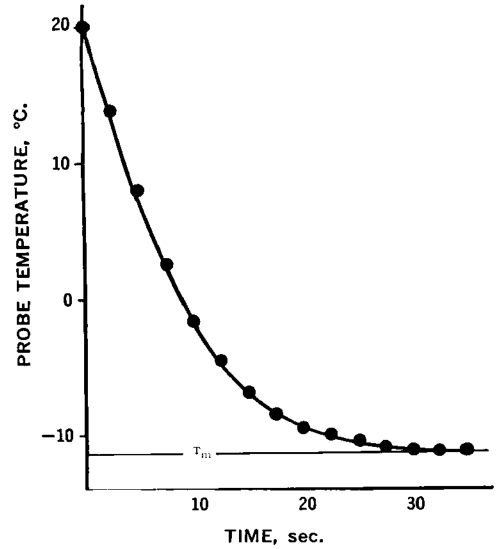

Figure 2—*Cooling curve for Propellant 12 (dichlorodifluoromethane)*

INTERPRETATION OF COOLING CURVES

If the sensor probe is small it can be assumed that the difference between the temperature of the spray at the probe and the temperature (T_m) obtained from the cooling curve is negligible. Furthermore, if the rate determining step in the heat transfer between the spray and the probe is conduction through the spray, it can be assumed that the instantaneous cooling rate of the probe at time t is proportional to the difference between the temperature of the probe T_t at time t and the temperature of the spray T_m.

Thus,

$$\frac{-dT_t}{dt} = k(T_t - T_m) \qquad \text{(Eq. 1)}$$

Integrating this equation between initial probe temperature T_0 and probe temperature T_t at time t we get:

$$\log \frac{T_0 - T_m}{T_t - T_m} = \frac{kt}{2.303} \qquad \text{(Eq. 2)}$$

Thus, $T_t - T_m$ decreases exponentially with time. The constant k representing the first-order cooling rate constant can be calculated from the plot of log ($T_t - T_m$) *versus* t obtained from the cooling curves. The cooling half-life ($t_{0.5}^{c}$) is related to the first-order cooling rate constant by the relationship:

$$k = 0.693/t_{0.5}^{c} \qquad \text{(Eq. 3)}$$

A typical cooling curve obtained for an aerosol propellant is shown in Fig. 2.

Figure 3 shows a plot of log ($T_t - T_m$) *versus* t for Propellant 12. The results show excellent agreement with the relation predicted by the mathematical model described before.

The value of k for a given aerosol formulation is dependent on the probe, the geometry of the test chamber, and the factors affecting the spray itself such as temperature, pressure, spray rate, and spray pattern. If these factors are kept constant, values of k can be used to compare the chilling effect of different aerosol formulations on a relative basis.

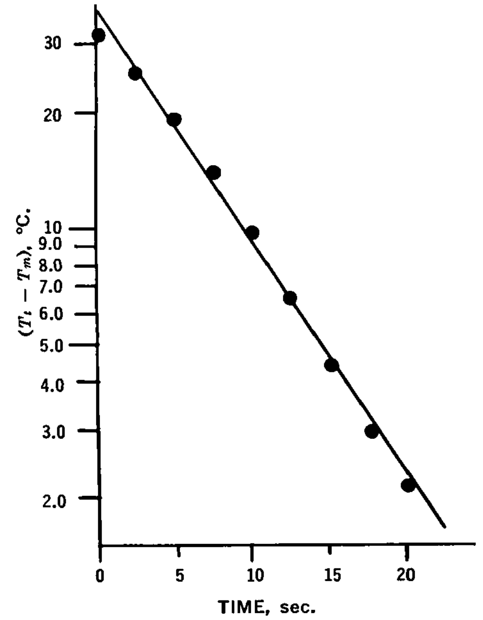

Figure 3—*Chilling effect of Propellant 12 (dichlorodifluoromethane).*

Table I—Chill-Index and Minimum Probe Temperature Values for Some Commonly Used Aerosol Propellants

Propellant[a]	Chill Index, °C./sec.	Minimum Probe Temp. (T_m), °C.
12	6.61	−11
12/11 (75/25)	3.73	−11.5
12/11 (50/50)	7.9	−16
12/11 (25/75)	6.48	−18
12/114 (40/60)	10.7	−16.5
152a	1.65	−39

[a] Nomenclature: propellant 11, trichlorofluoromethane; propellant 12, dichlorodifluoromethane; propellant 114, dichlorotetrafluorethane; propellant 152a, difluoroethane.

CHILL-INDEX CONCEPT

It is clear from the first-order behavior in cooling of the probe, that the temperature of the spray is not the only factor affecting the chill produced by the spray. Different sprays which have the same T_m values but have widely different k values will obviously have different chilling effects. It might, therefore, be proper to introduce the quantity chill index which represents the instantaneous cooling rate of the specified probe at normal human body temperature (37.5°) when exposed to the spray according to the procedure described.

The values for chill index can be used for comparative quantitative evaluation of chilling effects of different aerosol sprays.

Table II—Effect of Addition of Ethanol, Isopropanol, and Acetone on the Chilling Effect of Aerosols Made with Propellant 12/114 (40/60)

Additive	Amt. of Additive, %	Chill Index, °C./sec.	T_m, °C.
None	0	10.6	−16.4
Ethanol	2.5	8.7	−9.2
	5	9.5	−3.5
	10	10.9	2
	15	11.8	5.3
	20	12.4	5.2
	25	11.0	7.0
	30	10.0	9.2
Isopropanol	2.5	8.1	−6
	5	7.4	0.4
	10	5.8	0.5
	20	10.6	6.8
	25	11.1	7.2
	30	12.9	7.6
Acetone	2.5	8.5	−12.6
	5	11.2	−19.7
	10	11.2	−13.9
	15	10.8	−7.5
	20	17.3	−9
	25	18.4	−9
	30	12.4	−4

Table III—Effect of Addition of Ethanol on the Chilling Effect of Aerosols Made with Propellant 152a

Additive	Amt. of Additive, %	Chill Index, °C./sec.	T_m, °C.
None	0	1.65	−38.9
Ethanol	2.5	9.5	−37.5
	5.0	17.1	−31.6
	10.0	10.0	−27.8
	15.0	7.55	−17.0
	20.0	7.40	−6.4
	25.0	6.51	−8.4
	30.0	8.41	−5.0

The mathematical relationship between chill index (I_c), first-order cooling rate constant k of the probe, cooling half-life $t_{0.5}^c$ of the probe, the minimum temperature reached in the cooling curve T_m and the normal body temperature T_n is expressed as follows:

$$I_c = k(T_n - T_m) = 0.693\,(T_n - T_m)/t_{0.5}^c \qquad \text{(Eq. 4)}$$

Chill-index values for several aerosol propellants were determined. These are listed along with the minimum probe temperature values in Table I.

The effect of addition of varying amounts of ethanol, isopropanol, and acetone on the chilling effect of Propellant 12/114 (40:60) is indicated in Table II. The effect of addition of varying amounts of ethanol on the chilling effect of Propellant 152a is indicated in Table III.

The relationship between the chill-index value of the propellant additive mixture and the concentration of the additive is complex. An increase in the concentration of the additive not only alters the thermal characteristics of the spray but also alters the spray rate and the spray pattern due to changes in the vapor pressure, viscosity, surface tension, and density.

It may be observed that addition of increasing quantities of ethanol, isopropanol, or acetone to an aerosol propellant generally results in a rise in the chill index which tends to level off or even decrease with the further increase in the concentration of the additive.

Chill index values and minimum probe temperature values of some commercial aerosol products are indicated in Table IV.

A fair correlation was noted between panel observations on chilling effect and the observed chill index values. Additional studies aimed at utilizing this new tool in the evaluation of aerosol products are currently in progress.

Table IV—Chill Index and Minimum Probe Temperature Values of Some Commercial Aerosol Products

Type	Product	Chill Index, °C./sec.	T_m, °C.
Anesthetic Skin Refrigerant	A	12.2	−25.6
Deodorant	B	9.9	10.3
Deodorant	C	6.3	11.3
Deodorant	D	11.0	10.5
Deodorant	E	5.76	4.2
Wound dressing	F	18.7	−13.2
Wound dressing	G	6.1	−6.6
Spray antiseptic	H	13.5	2

SUMMARY

Instrumentation—The instrumentation used for obtaining the cooling curves for the aerosol sprays consisted of a test chamber, a thermistor probe, a thermistor telethermometer, and a fast-response strip-chart recorder.

Calculation of Chill Index—Chill index of an aerosol spray is calculated from the first-order cooling rate constant obtained from the cooling curve and represents the instantaneous cooling rate of the probe at 37.5°.

Chilling Effect of Some Common Aerosol Propellants—Chill index values for some common aerosol propellants and propellant blends were determined. The effects of addition of ethanol, isopropanol, and acetone on the chill index values of Propellant 12/114 (40:60) and of addition of ethanol to Propellant 152a were investigated.

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