XIII_481

Theor. Appl. Climatol. 45, 155–159 (1992)

Theoretical and Applied Climatology

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Weather Modification Reagents.
I. On the Presentation and Interpretation of the Cold Chamber Ice-Nucleating Reagent Activity Measurement

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With 6 Figures

Received April 30, 1991

Summary

New activity coefficients for ice-forming characteristics of the pyro-technical mixtures are proposed. For activity-temperature relationship, we propose the following empirical expression:

$$\log A = \frac{B_1 \cdot \text{temperature}}{B_2 + \text{temperature}}$$

where, A – number of created ice crystal per gram pyrotechnical mixture,
B_1 – maximum activity of the reagent,
B_2 – temperature at which the activity has half of its maximum value.

Therefore, the B_1, B_2 and B_2/B_1 coefficients show potential use in the describing of the activity of ice nucleating reagents. The above equation is transformed algebraically into other forms that are more useful for plotting experimental data. One of the most convenient transformations is

$$\frac{\text{temperature}}{\log A} = \text{intercept} + \text{slope} \cdot \text{temperature}$$

B_1 and B_2 may be evaluate as $B_1 = \frac{1}{\text{slope}}$ and $B_2 = \frac{\text{intercept}}{\text{slope}}$

This method does has a potential application for the quantitative presentation and interpretation of cold chamber ice-nucleating reagents activity measurements since it permits rapid, precise, accurate and low-cost analyses.

1. Introduction

The activity of reagents is measured in several type of cold chambers. Figure 1 shows the traditional way of presentation of ice-nucleating pyro-technical mixture activity (Horvat, 1989).

Obviously, it is of interest therefore to explore the possibilities for using mathematical and statistical methods for the presentation and interpretation of the cold chamber ice-nucleating reagents activity measurements. In addition, this method might be used to evaluate the activity of ice-nucleating reagents.

The aim of this paper is to develop a new empirical and statistically reliable equation to express the dependence of experimental data of the cold chamber ice-nucleating reagents activity measurement. We proposed new reagent activity coefficients B_1, B_2 and B_2/B_1. It is hoped that this general approach will find further application in the presentation and interpretation of the reagents activity.

2. Results and Discussion

Experimental data used in this theoretical approach were obtained at the Hydrometeorological Institute of Croatia, Zagreb (Horvat, 1989), for the pyrotechnical mixture R-32, VTG-8 (NIBK, Vinča, Yugoslavia), MKM-10 ("Poliester", Priboj, Yugoslavia) and AJ ("Makpetrol-Temko", Skopje, Yugoslavia). The observed experimental pyrotechnical mixture activity were fitted to many log A vs temperature equations by a least-squares regression method using the Statgraphics Computer

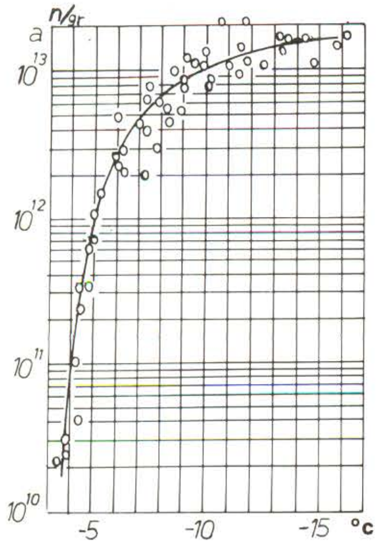


Fig. 1. AJ pyro-technical mixture activity. Traditional way of presentation (Horvat, 1989)

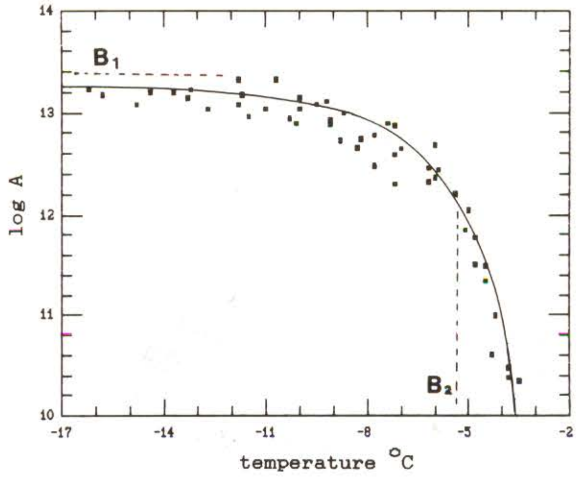


Fig. 2. Effect of temperature on the reagent activity A, expressed as a logarithm of number of created ice crystal per gram pyro-technical mixture; B_1 – maximum activity of the reagent, B_2 – it expresses the temperature at which the activity has half of its maximum value

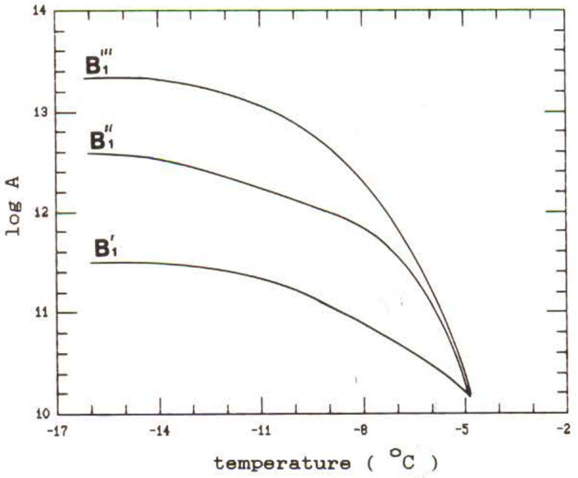


Fig. 3. Temperature – log A curves for three types ice-nucleating reagents (deviation in B_1 coefficients)

Program (Statgraphics manual, 1988). We find that Eq. (1) is a statistically expression to represent the dependence of experimental data of cold chamber ice-nucleating reagents activity measurements.

$$\log A = \frac{B_1 \cdot \text{temperature}}{B_2 + \text{temperature}} \tag{1}$$

This equation defines the quantitative relationship between the ice-nucleating reagent activity and temperature if both coefficients B_1 and B_2 are known.

The general principles of mathematics are applicable to this relationship. In Fig. 2 we see the effect of temperature on the reagent activity. At high temperature (about $-3\,^\circ\text{C}$ to $-6\,^\circ\text{C}$), the activity log A is proportional to the temperature. However, as the temperature is decreased, the reagent activity falls off and is no longer proportional to the temperature. With further decrease in temperature, the activity becomes constant and independent of temperature. We refer to this point (coefficient B_1) as the maximum activity of the reagent. All ice-nucleating reagents show this point, but they vary widely (Fig. 3) and there are specific coefficients for each reagent. B_1 has the dimension of numbers of created ice crystal per gram pyro-technical mixture.

An important numerical relationship emerges from the Eq. (1) in the special case when $\log A = B_1/2$. We then have

$$\frac{B_1}{2} = \frac{B_1 \cdot \text{temperature}}{B_2 + \text{temperature}} \tag{2}$$

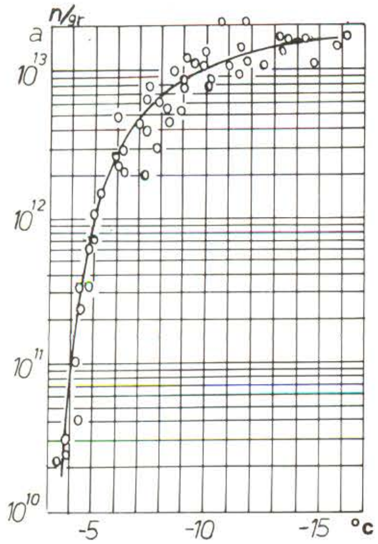
If we divide by B_1, we obtain

$$\frac{1}{2} = \frac{\text{temperature}}{B_2 + \text{temperature}} \tag{3}$$

Rearranging,

$$\begin{aligned} B_2 + \text{temperature} &= 2 \cdot \text{temperature} \\ B_2 &= \text{temperature} \end{aligned} \tag{4}$$

We may therefore conclude that B_2 is equal to the temperature at which the ice-nucleating activity



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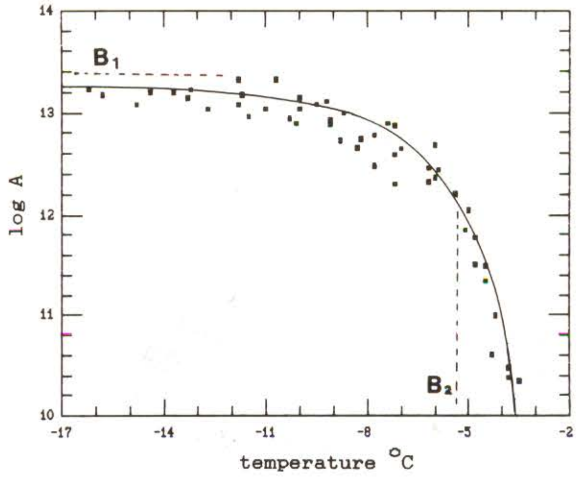

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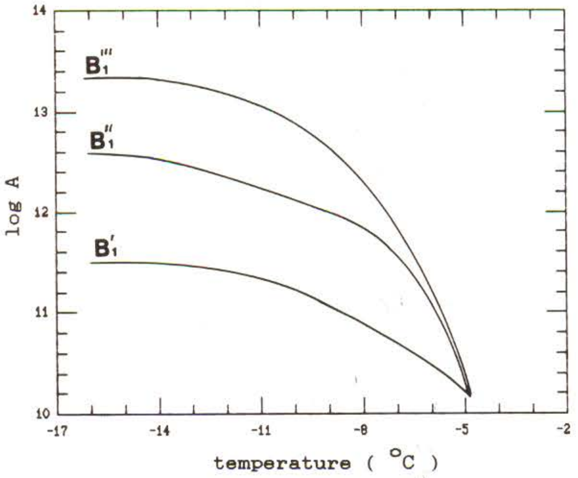

Fig. 3. Temperature – log A curves for three types ice-nucleating reagents (deviation in B_1 coefficients)

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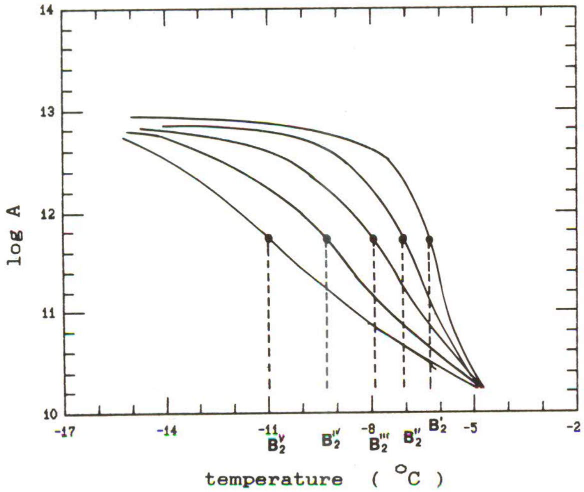

Fig. 4. Temperature – log A curves for fifth types ice-nucleating reagents (deviation in B_2 coefficients)

has half of its maximum value. Obviously, B_2 has the dimension of temperature.

Figure 2 shows that B_2 can be extrapolated graphically from data on the effect of temperature on the reagent activity ($\log A$). Note that B_2 is not a fixed value, it may vary with the reagent performance and each reagent has a characteristic B_2 coefficient (Fig. 4). B_2/B_1 ratio is also a very important descriptor of reagent activity properties. Reagents with relatively large B_2/B_1 ratios are "reagents with a broad spectrum of action". Otherwise, they are "reagents with limited threshold activity". In addition, the results from cold chamber ice-nucleating reagents activity measurements, obtained by different researchers have different values, but comparison of B_2/B_1 ratio values for the same reagent come from different cold chambers should be quite similar. Therefore, B_1, B_2 and B_2/B_1 coefficients can be used in the evaluation of the activity of ice-nucleating reagents.

3. Application of Equation (1)

Experimental data used in this theoretical approach were according to Horvat (1989), for the pyro-technical mixture R-32, VTG-8 (NIBK, Vinča), MKM-10 ("Poliester", Priboj) and AJ ("Makpetrol-Temko", Skopje). The results obtained on the application of Eq. (1) for B_1, B_2 and B_2/B_1 estimation are presented in Table 1. We can see, according to the B_1 coefficients that pyro-technical mixture VTG-8 is most active; according to the B_2 coefficient, the most active is MKM-10, but the B_2/B_1 ratio values suggest that the pyro-technical mixture MKM-10 and AJ proved to be more active than R-32 and VTG-8 in the relatively wide temperature range. This explanation is slightly different than Horvat's (1989), but have showed good agreement.

Table 1. *B_1, B_2 and B_2/B_1 Coefficients Values for some Ice-Nucleating Reagents Using Eq. (1)*

Reagent*	B_1	B_2	B_2/B_1	r	F
AJ	14.60	-1.25	-0.0856	0.940	$48860^{2.48}$
R-32	14.88	-1.73	-0.1163	0.938	$39206^{2.43}$
MKM-10	13.91	-0.70	-0.0503	0.910	$98676^{2.34}$
VTG-8	15.78	-2.51	-0.1591	0.952	$54900^{2.48}$

* Experimental data according to Horvat (1989)

4. Transformation of the Equation (1)

The Eq. (1) can be transformed algebraically and tested statistically into other forms that are more useful in plotting experimental data (Bogdanov, 1991), for example Eq. (5) to Eq. (8):

$$\frac{1}{\log A} = \frac{B_2 + \text{temperature}}{B_1 \cdot \text{temperature}} \tag{5}$$

$$\log A = \text{intercept} + \text{slope}\,\frac{\log A}{\text{temperature}} \tag{6}$$

in Eq. (6): $B_1 = \text{intercept}$; $B_2 = -\text{slope}$

$$\frac{1}{\log A} = \text{intercept} + \text{slope}\,\frac{1}{\text{temperature}} \tag{7}$$

in Eq. (7): $B_1 = 1/\text{intercept}$; $B_2 = \text{slope}/\text{intercept}$

$$\frac{\text{temperature}}{\log A} = \text{intercept} + \text{slope}\cdot\text{temperature} \tag{8}$$

in Eq. (8): $B_1 = 1/\text{slope}$; $B_2 = \text{intercept}/\text{slope}$.

A statistical evaluation of the above various graphical methods for determining B_1 and B_2 shows that the Eq. (8) (Fig. 5) is the most satisfactory and gives the most accurate values of these quantities over the usual range of temperature and reagent activity available from experimentation on cold chamber ice-nucleating reagents activity measurement.

This equation has a high r and very small standard deviation (Table 2).

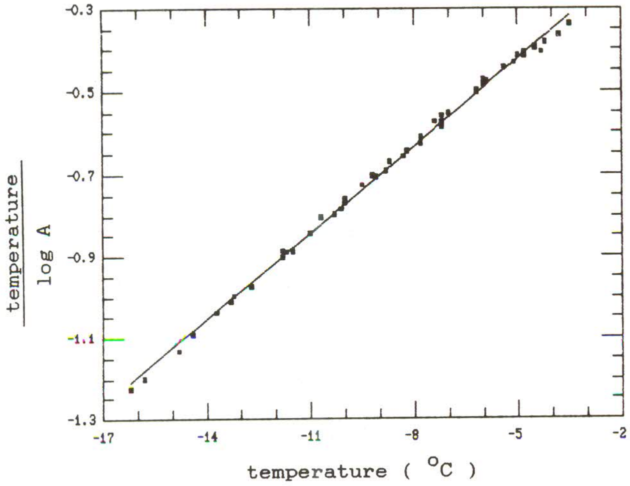

Fig. 5. Plot of the temperature/log A versus temperature according to Eq. (8). $B_1 = 1/\text{slope}$; $B_2 = \text{intercept}/\text{slope}$

Table 2. *B_1, B_2 and B_2/B_1 Coefficients Values for some Ice-Nucleating Reagents Using Eq. (8)*

	Reagent*			
	AJ	R-32	MKM-10	VTG-8
Slope	0.0702	0.0690	0.0724	0.0653
Intercept	−0.0720	−0.0998	−0.0469	−0.1418
r	0.9986	0.9973	0.9990	0.9960
F	$17605^{1,48}$	$8050^{1,43}$	$16319^{1,34}$	$5913^{1,48}$
B_1	14.29	14.49	13.82	15.31
B_2	−1.03	−1.45	−0.65	−2.17
B_2/B_1	−0.072	−0.100	−0.047	−0.142

* Experimental data according to Horvat (1989)

Although it might be not inferior to Eq. (1) in term of B_1 and B_2 evaluate quality, it has the advantage that B_1 and B_2 can be easily calculated from the straight line with a slope of $1/B_1$ and an intercept of B_2/B_1 and of $-B_2$ on the ordinate and on the abscissa, respectively, without having any statistical computer package.

In our calculation not all of fifty experimental data are necessary to be used for B_1 and B_2 evaluate. The results of this study suggested that an analyst can measure the ice-nucleating reagents activity of only several temperatures, plot the straight line and evaluate the B_1 and B_2 coefficients. The question is, how many experimental data are needed to generate the equation in order to get reasonably accurate coefficients values? To answer this question, we have performed the following experiment to determine the size of the subset required.

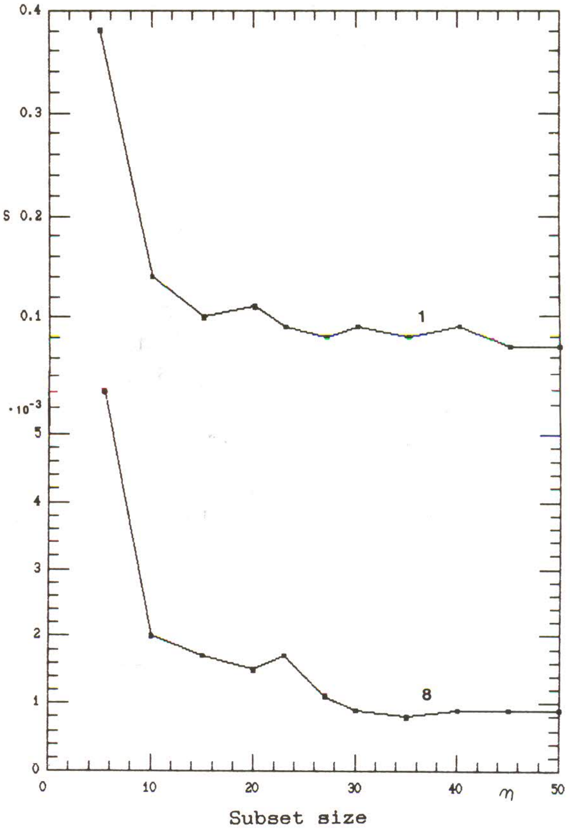

Fig. 6. Standard deviation (s) vs subset size (n). Curves 1 and 8 show the results based on Eq. (1) and Eq. (8), respectively

Ten training sets were generate by randomly selecting n experimental data from the fifty available full data set. For each training set an equation was developed by using the Eq. (1) and Eq. (8). The equations were then used to evaluate B_1 and B_2 coefficients. Comparisons were made against full set values, and the residual mean square were calculated as a measure of precision. The procedure was repeated with n values between 5 and 50.

The results of these experiment can be best described by plotting the standard deviation (s) against the size of the subset (Fig. 6).The s value decreases rapidly as n increases and stabilizes when n is about 10. Thus, a subset of $10/50 = 20\%$ of the entire data set was sufficiently large to allow the generation of a equation of high quality. It is obvious (Fig. 6) that Eq. (8) is more satisfactory and gives the more accurate values for B_1 and B_2 coefficients than Eq. (1). In this particular experiment, the mean value of s for $n = 10$ observations (0.00283) is almost the same as the standard error of fitting the whole data set. When this experiment was repeated using different training sets, and the standard deviation was plotted against n, a curve of a similar shape was obtained. Again the minimum size of the subset was about 10.

5. Conclusion

B_1, B_2 and B_2/B_1 coefficients from Eq. (1) or Eq. (8) are suitable for the evaluation of the activity of ice nucleating reagents. The method does have the potential for application to the quantitative presentation and interpretation of cold chamber ice-nucleating reagents activity measurements since it permits rapid, precise, accurate and low-cost analyses.

Acknowledgements

The author wishes to thank V. Horvat (Zagreb, Yugoslavia) and D. Ančovski (Skopje, Yugoslavia) for helpful discussions on this topic.

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Verleger: Springer-Verlag KG, Sachsenplatz 4—6, A-1201 Wien. — Herausgeber: Prof. Dr. I. Dirmhirn, Universität für Bodenkultur, Institut für Meteorologie und Physik, Türkenschanzstraße 18, A-1180 Wien. — Redaktion: Türkenschanzstraße 18, A-1180 Wien. — Satz und Umbruch: Thomson Press (India) Ltd., New Delhi. — Reproduktion und Offsetdruck: Druckerei G. Grasl, A-2540 Bad Vöslau. — Verlagsort: Wien. — Herstellungsort: Bad Vöslau. — Printed in Austria.