Apparatus for Direct, Rapid Determination of Saturation Temperatures for Liquid Fertilizers Using Dauncey and Still's Optical Method

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An apparatus has been constructed to measure saturation temperatures of liquid fertilizers, down to −30° C., using Dauncey and Still's optical method. A large crystal or pellet of compressed salt is used. The accuracy is about ±0.5° C. The method has been extended to dilute liquid fertilizer solutions, a small ice cube being used instead of a crystal. In this case the accuracy is about ±0.03° C. It is possible to work out the complete solubility curve of a liquid fertilizer, at the rate of several measurements an hour, which is much faster than standard methods.

An important physical characteristic of liquid fertilizers is their saturation temperature, which determines the possibility of their crystallizing when in cold storage. There are few standard methods for determining these temperatures. The polythermal method—also called the "cloud method" (*9–12, 14*)—and the isothermal method (*10–12*) may be mentioned in particular. The chief disadvantage of these two methods is their slowness; the polythermal method requires at least a few hours, and the second method at least a few days.

There is a new method, however, developed by Dauncey and Still (*3*), based on an optical phenomenon. The author has applied this optical method to liquid fertilizers, and constructed an apparatus which can work at temperatures down to − 30° C. and also above room temperature. The use of this method also has been extended to dilute solutions for which the crystalline phase apparent during cooling is ice. The possibility of using the method in this way does not seem to have been mentioned elsewhere.

Dauncey and Still's Optical Method

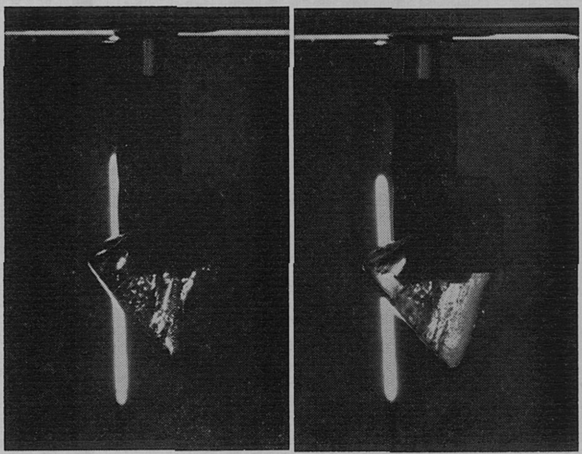
Dauncey and Still discovered this method while doing research on the growth of large crystals of compounds soluble in water.

Principle of the Method. The method is based on an optical effect caused by the slight difference in concentration, and, therefore, in the index of refraction between the solution and a thin layer of liquid in contact with a crystal, which is either dissolving or growing.

Optical Effect Recorded. Let us consider a crystal submerged in the solution to be examined, observing one side of it, lit from behind through a luminous slit, in the axis of observation (Figure 1). If the crystal is dissolving, the luminous line from the slit presents appearance 1 (Figure 1), running along the side of the crystal and making an obtuse angle. If the crystal is growing, the luminous line is broken in the other direction and makes an acute angle (view 3, Figure 1). If the crystal is at equilibrium—i.e., if the solution is saturated—there is no optical effect (view 2, Figure 1).

In the case of dilute solutions, in which a small piece of ice is submerged, the same images occur, but reversed (acute angle–obtuse angle).

The temperature of the solution is varied just enough to observe the two photographic images 1 and 3, and the two corresponding temperatures—which thus lie on each side of the saturation temperature—are noted. The saturation temperature is taken to be the average of these two temperatures.



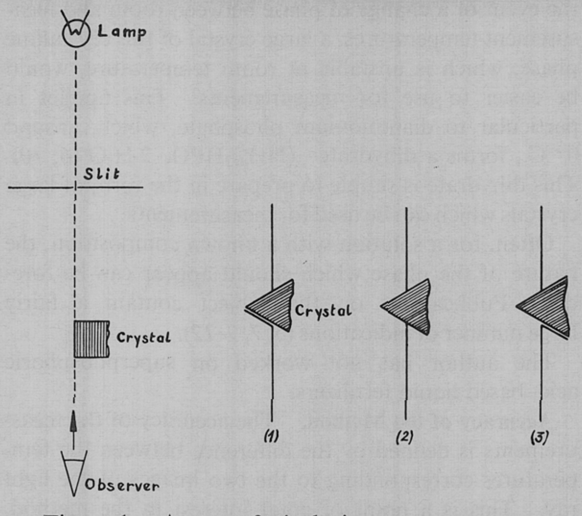


Figure 1. Aspect of slit during a measurement

1. Unsaturated, 2. Saturated, 3. Supersaturated

Photographs of view 1 (left) and view 3 (right)

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Explanation of Optical Phenomenon. Dauncey and Still, and Mullin (*8*) describe only the optical effect recorded. Further explanation is, however, easy, if it is noticed that the light passing through the slit is not parallel and if it is admitted that the thin film of liquid, which is observed in contact with the crystal—the existence of which was demonstrated (*1*, *2*)—has a form assimilable, for instance, to a half cylindrical lens, whose axis is perpendicular to the lamp-observer axis.

Therefore, the light coming from the slit is refracted in the film of liquid in contact with the crystal and is so directed to the observer. The latter is therefore able to see along the crystal, in one case the upper part of the slit masked by the crystal; in the other case, the lower part of the slit.

Field of Application of Method. A distinction will be made between the case of dilute solutions of liquid fertilizers, corresponding to the freezing curve where the crystalline phase is ice, and the case of concentrated solutions, where the crystalline phase which appears is a salt.

Dilute Solutions. In the field 0° C.–cryohydric point, a small ice cube is submerged in the solution. In this case, the method has very great sensitivity. The accuracy of measurements is approximately ±0.03° C. The method thus provides a simple, very rapid and accurate system of cryoscopy.

For each measurement, as soon as the temperature of the solution drops by a few tenths of a degree centigrade below the saturation temperature, the ice starts to crystallize in the solution, while a few tenths of a degree above, it redissolves. This is the polythermal method.

Concentrated Solutions. The method requires knowledge of the crystalline phase which should appear, or at least the possibility of taking a large crystal from this crystalline phase, during a preliminary crystallizing operation on the solution. Instead of a large crystal, as the authors of the method point out (*3*), a pellet prepared by compressing powdered salt can be used. In the event of a change of phase between room and measurement temperatures, a large crystal of this crystalline phase, which is unstable at room temperature, would be easier to use for measurements. This applies in particular to diammonium phosphate, which, around 0° C., forms a dihydrate—$(NH_4)_2HPO_4 \cdot 2\,H_2O$ (*6*, *10*). This dihydrate is simple to prepare in the form of large crystals which can be used for measurements.

Often, for a solution with a known composition, the nature of the phase which should appear can be forecast. Publications on the subject contain a fairly large number of indications (*5*, *7*, *9*–*12*).

The author has not worked on superphosphoric acid–based liquid fertilizers.

Accuracy of the Method. The accuracy of the measurements is defined by the difference between the temperatures corresponding to the two images of the light ray. This is a point of great interest in the method, since the accuracy of each measurement is thus known automatically.

Dilute Solutions. The accuracy is around ±0.03° C.

Concentrated Solutions. Dauncey and Still, and Wise and Nicholson (*13*), whose instruments Kelly (*4*) deals with in particular, indicate, respectively, an accuracy of ± 0.1°, or even ± 0.05° C., and ± 0.1° to ±0.2° C. They operated between about +20° and +80° C., especially on ethylenediamine tartrate solutions, monoammonium phosphate, and sugar solutions. In the case of liquid fertilizers, for temperatures around 0° C. or below, the accuracy is generally a little less.

In measurements with diammonium phosphate crystals or pellets, or crystals of diammonium phosphate dihydrate, on a solution of pure ammonium phosphate, or rich in ammonium phosphate, accuracy is about ±0.3° C. The same accuracy can be obtained in measurements using a plate of ammonium nitrate on urea–ammonium nitrate solutions.

With ternary fertilizers containing potassium chloride, measurements using a potassium chloride pellet give an accuracy of from ±0.8° to ±1° C., approximately. On the whole, the accuracy of the method may be estimated at about ±0.5° C. This accuracy is satisfactory for liquid fertilizers.

Equipment

Figure 2 shows the two basic parts: the measuring cell with internal circulation, *A*, which contains the liquid fertilizer and the lighting tube with the slit; and a bath which can be used to change the temperature of cell *A*.

Measuring Cell A. This is a stainless steel cell, measuring 14 × 10 × 4 cm. and holding about 400 ml. of solution. Two glass windows, 2.5 × 4.5 cm., are used for observation of the crystal or salt pellet, attached to tongs at the end of a rod, *a*. A baffle, *c*, facilitates the circulation of the solution, produced by a motor-driven propeller, *b*, of variable speed. A good agitation of the solution is needed to give good homogeneity of temperature. Dauncey and Still also underline this point. A precision thermometer, *t*, gives the temperature of the liquid near the crystal.

Lighting Tube and Slit. This consists of a 4-cm. diameter tube, closed at the end by a disk with a slit, *F*, about 0.2 to 0.3 mm. wide. In the middle is a disk of Plexiglas, unpolished, and at the other end, in a bulb, a 220-volt–40-watt lamp. The tube is about 25 cm.

Refrigerated Bath. The measuring cell, *A*, is placed in a second tank of poly(vinyl chloride), measuring about 24 × 10 × 17 cm. and containing a calcium chloride solution, stirred by a motor-driven propeller, *d*. This solution is refrigerated by the evaporator, *E*, of a $^1/_4$-hp. refrigerating unit, linked to it by a flexible pipe. A temperature of −20° C. can be attained in about 2 hours, and −30° C. in about 3 hours.

The unit is controlled by a contact thermometer, *T*, and the refrigerating power can also be reduced by a valve controlling the vaporization of the Freon in the evaporator, *E*. A heating resistance, *R*, of 220 volts–300 watts under a tube of cast silica is used to heat the liquid.

This cell also has two double windows, *B*, for ob-

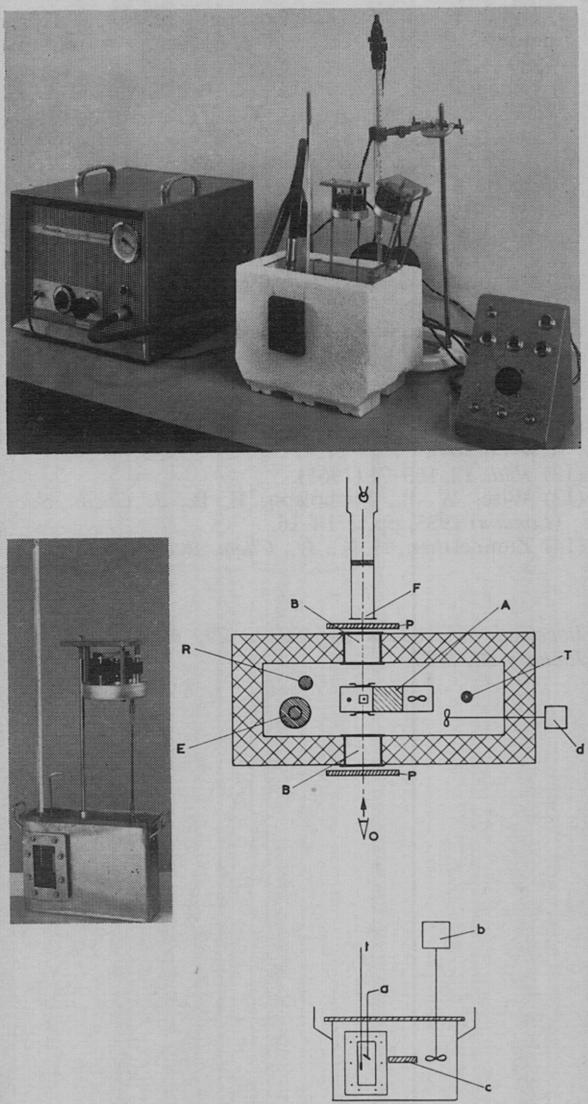

Figure 2. Photographs and diagram of experimental equipment

- *A.* Measuring cell
  - *a.* Rod
  - *b.* Motor-driven propeller
  - *c.* Baffle
  - *t.* Precision thermometer
- *B.* Double windows
- *E.* Evaporator of refrigerating unit
- *F.* Slit
- *O.* Observer
- *P.* Heating resistances
- *R.* Heating resistance, 220 volts/300 watts
- *T.* Contact thermometer
- *d.* Motor-driven propeller

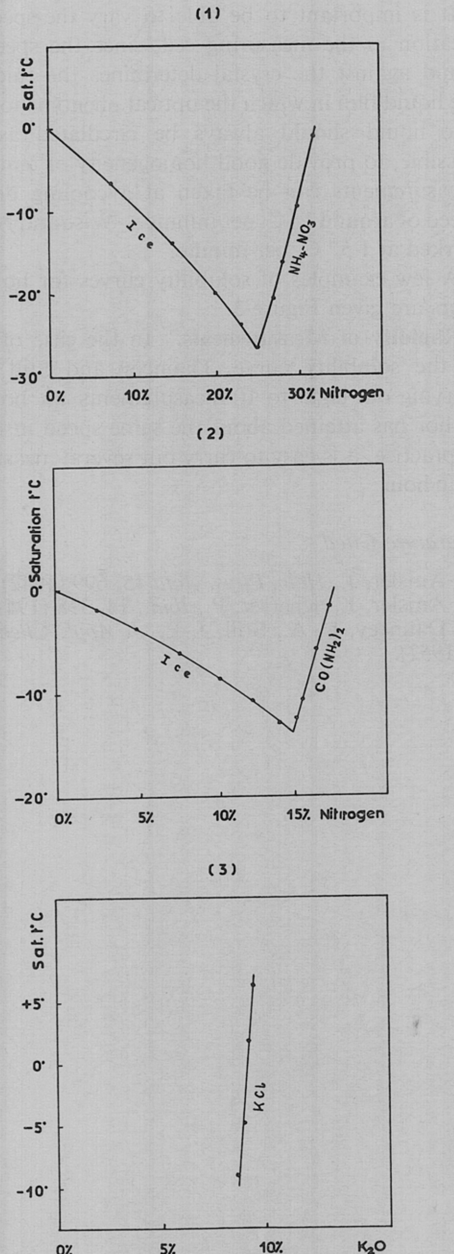

Figure 3. Solubility curves for liquid fertilizers

(1) Fertilizer X–O–O
$[NH_4 \cdot NO_3–CO(NH_2)_2–H_2O]$

(2) Fertilizer 2–I–O
$[NH_3–H_3PO_4–CO(NH_2)_2–H_2O]$

(3) Fertilizer I–I–I
$[NH_3–H_3PO_4–CO(NH_2)_2–KCl–H_2O]$

servation of the crystal. Two small heating resistances, *P*, prevent the formation of misting on the outside windows. The whole cell unit is heat-insulated by 3-cm. thick expanded polystyrene.

Taking Measurements. First, one must have the crystal or pellet for placing in the apparatus. In the case of a crystal, the surface to be observed need only be a few millimeters square.

For routine measurements, it usually will be easier to prepare a pellet, about 10 mm. in diameter and 2 mm. thick, for example, by compressing powdered salt. The author has prepared such pellets with mono- and diammonium phosphate, potassium chloride, and urea. In the case of ammonium nitrate, a plate can be prepared by fusion.

For dilute solutions, the ice cube can be prepared easily in a mold measuring about 8 × 8 × 4 mm., into which is inserted a small rod about 2 cm. long, making it simpler to manipulate the cube and fix it on to the tongs in the apparatus.

It is important to be able to vary the speed of circulation in the measuring cell, since the speed of the liquid against the crystal determines the thickness of the liquid film in which the optical phenomenon occurs. The liquid should always be circulated as fast as possible, to provide good homogeneity of temperature. Measurements can be taken at a cooling or heating speed of around 1° C. per minute. Wise and Nicholson worked at 1.5° C. per minute.

A few examples of solubility curves for liquid fertilizers are given Figure 3.

Rapidity of Measurements. In the case of a graph of the solubility curve, Dauncey and Still mention carrying out eight to 10 measurements an hour. The author has attained about the same speed in this case. In practice, it is easy to carry out several measurements in an hour.

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