DETERMINATION OF IMPURITIES IN WATER
FROM OBSERVATION OF FREEZING TEMPERATURE

Jon A. Peterka

Advised by

Dr. richard A. Schleusener

Study conducted under
NSF Undergraduate Research Participation Program - 1960

Civil Engineering Section
Colorado State Unviersity
Fort Collins, Colorado

January 1961

CER61JAP1

DETERMINATION OF IMPURITIES IN WATER FROM OBSERVATION OF FREEZING TEMPERATURE OF SMALL DROPS

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I. INTRODUCTION

It has been determined that a sample of water will not always freeze at 0°C. Both the percent of impurities and the volume of the sample influence the temperature at which the sample freezes small drops of distilled water will freeze at varying temperatures depending on the volume of water in the drop. The smaller the drop, the lower the temperature. A drop with a diameter of 10 microns will freeze at approximately -40°C. Drops of the same volume will freeze at approximately the same temperature. Impurities in a drop tend to raise the freezing temperature slightly by providing a nucleus around which ice crystals can form. By experimentally freezing droplets of the same volume and comparing the mean freezing temperature of a particular sample with the mean freezing temperature of a control sample, the concentration of impurities can be calculated.

II. OBJECTIVES

My assignment was to further develop a freezing technique for small water droplets which Dr. Schleusener observed in California. The method was to inject small droplets of water into the interface between two liquids - carbon tetrachloride and mineral oil - one being heavier and the other being lighter than the water droplets. The purpose of the assignment was to obtain a workable method for the freezing of small water droplets so that the amount of impurities in the sample could be determined.

III. PROCEDURE

This is the method that has been developed for finding the mean temperature of the freezing points of droplets of water which are 1.0 mm and 0.5 mm in diameter. The small drops are suspended in the interface between carbon tetrachloride and mineral oil - the mineral oil being above the drops and the carbon tetrachloride below the drops. A thermister - a resistance thermometer - is inserted into the interface and the cup containing the liquids is cooled. Over each determined increment of temperature, the number of drops that freze during that temperature range and the time required for the cooling through the increment are recorded. From this data the mean temperature of the freezing points of the drops and the rate of cooling can be plotted.

Preparation of Materials

The first step is to prepare the materials. Some of the clear carbon tetrachloride should be poured into a small wide-mouth bottle and Sudan IV - an organic dye - added until the solution is nearly saturated. Sudan IV is available in the Physiology Department. The next step is to coat the bottom of one of the aluminum cups with India ink to obscure the texture. Approximately 5 ml of the dye solution (about 3/16") is poured into the cup. If light can be seen reflecting from the bottom of the cup, the bottom should be recoated with ink. To keep it from mixing with the cc/4, the oil should be made to run down the side of the cup. The time lapse between the addition of the cc/4 and the addition of the oil should be fairly short to minimize the evaporation of the cc/4. Once the mineral oil has been added, the cup should not be moved excessively. It will help to preserve the interface. Add mineral oil until the cup is slightly less than half full. Squibb brand mineral oil is the best to use because it does not become cloudy while cooling. The mineral oil available through the Chemistry Department should not be used because it does become cloudy with cooling.

Production of Droplets

The next step is the production of the droplets. Insert the small syringe #902 into the center hole of a #12 rubber stopper and place the stopper in a 3" ring attached to a ring stand. The syringe is now in a vertical position pointing downward. A #29 needle is attached to the syringe. The tip of the needle should be cut off square and filed smooth on sandpaper. The 15-power magnifier should be removed from its mount and held on the ring-stand by means of a clamp. By adjusting the clamp, the magnifier can be focused on the tip of the needle. The next thing to do is to remove the plunger of the syringe, slip 1/4" of rubber hose over it, and replace the plunger. Tape the rubber hose to the top of the syringe. This hose grips the plunger slightly and helps control it. Now remove the needle, and fill the syringe by immersing the end in the water to be tested and pulling out on the plunger. Not more than 1/2" to 3/4" of water should be in the syringe at one time. (It will make production of the drops easier.) Fit the needle back on the tip of the syringe and press the plunger slightly to fill the needle with water. If there are air pockets in the syringe or needle, they should be removed to make drop production easier. Adjust the magnifier and its scale so that the view through the magnifier appears similar to Fig. 1. Slowly push and pull the plunger while looking through the magnifier until the drop is 10 of the smallest units across (this is for 1.0 mm drops - for 0.5 mm drops, the drop should span 5 of the smallest markings). At this point the cup containing the cc/4 and mineral oil is brought up under the needle and raised until the end of the needle, with the droplet on it is submerged in the mineral oil as in Fig. 2. Then lower the cup straight down to bring the needle tip out of the oil. The 1.0 mm drop will remain in the oil. One precaution is important. The drop will tend to change size between the time it is last observed and the time it is released in the oil. To prevent this, the drop should be observed for several seconds through the magnifier after the plunger has been released. Once the drop is steady, the cup may be brought up to release the drop. After putting the drop in the oil, the tip of the needle must be wiped clean with a piece of clean cloth before making the next drop. It will be noticed that most of the droplets will sit just under the oil surface - unable to break the surface tension of the oil, as in Fig. 2. Touching them gently with a pointed object will break the surface tension and permit the drops to fall to the interface.

Positioning of Droplets in Container

Fig. 3 shows the positioning of the drops with respect to the thermistor. They should fall within the shaded area on the right. If they are positioned outside the shaded area, observation in the freezer becomes difficult. Positioning should be done as the drops are being produced. Fifteen drops may be put into the shaded area without crowding. The drops have little tendency to collect, but if two drops are too close together, they sometimes

Figures 1 & 2

Figures 3 + 4

combine into one. Once the drops are in the cup, their size may be checked by setting the cup on the base of the ringstand and focusing the magnifier on the drops in the interface and comparing them to the scale in the magnifier. The error should not be more than ± .025 mm.

Positioning of Thermistor

The next step is to put in the thermistor (see Fig. 3). Its holder is a piece of balsa which fits over the lip of the cup. The glass probe with the thermistor in the tip is then pushed through a hole in a short piece of hose that is slit lengthwise and then through the hole in the piece of balsa. The rubber hose permits the thermistor (the black spot in the tip of the probe) to be adjusted to any height. It should be adjusted so that it is at the interface of the two liquids. The two leads are then attached to the tacks on the sides of the balsa. Two short leads are also attached to the tacks. Once assembled, the thermistor and the balsa can be used as one unit. They can be attached to and removed from the cup without separating them.

Equipment in Freezer

The equipment in the freezer consists of a ring stand, a ring, a mount for a polaroid lens, a small piece of sheet metal, a ring of polyethylene, and a trouble light. The ring is attached near the top of the stand and the sheet metal placed across it. The ring of polyethylene - used to support the cup - is frozen to the center of the sheet metal. A polaroid plate is attached to the ring stand so that it is slightly above and behind the cup and set at approximately a 60° angle (see Fig. 4) The trouble light can be supported at about the right height by hanging it on one of the baskets in the freezer. The cup with the drops can now be placed on the sheet metal inside the polyethylene ring with the thermistor unit placed so that the leads extend toward the ring support. Two wires leading to a bridge should be fastened to these two leads. At this point the component positions should be checked. Turn on the light and move it slightly until the observer sees no reflection from the liquids in the droplet area. The water drops should not be visible.

Temperature Measurement with Resistance Bridge

For temperature measurement, an electrical bridge is used. Attach the thermistor wires to the unknown terminals, a 1-1/2 volt battery to the battery terminals, and CSU #15765 and Physics #3121 center reading galvanometer to the galvanometer terminals of the bridge. If this galvanometer is not available, any center reading galvanometer with a sensitivity of 0.5 to 1.0 microammeters per mm scale division is satisfactory. The bridge, a Minneapolis Honeywell Model 1090, is set to the ohmage which corresponds to the temperature desired as determined by the calibration curve of the thermistor. When the galvanometer shows no deflection, the desired temperature has been reached.

Data Recorded

At every 1/2°C the number of drops that are frozen is recorded along with the time necessary for the 1/2°C change. To note how many drops are frozen, turn on the light and move it around as before to eliminate reflections. If any drops are frozen, they will show up as small white spots which can be counted easily.

IV. RESULTS

The primary product of the summer's work is a workable method of freezing water drops. This procedure has been previously described.

Included also are the results of six water samples. The percent of drops frozen has been plotted against temperature for both sizes of drops. The sheets on which the original data was recorded contain the number of drops frozen at each half degree centigrade over the freezing interval, the time in minutes for some temperatures measured from the preceding even hour, total drops frozen in one-half degree interval, difference between successive total drop recordings, and the total drops expressed as a percentage.

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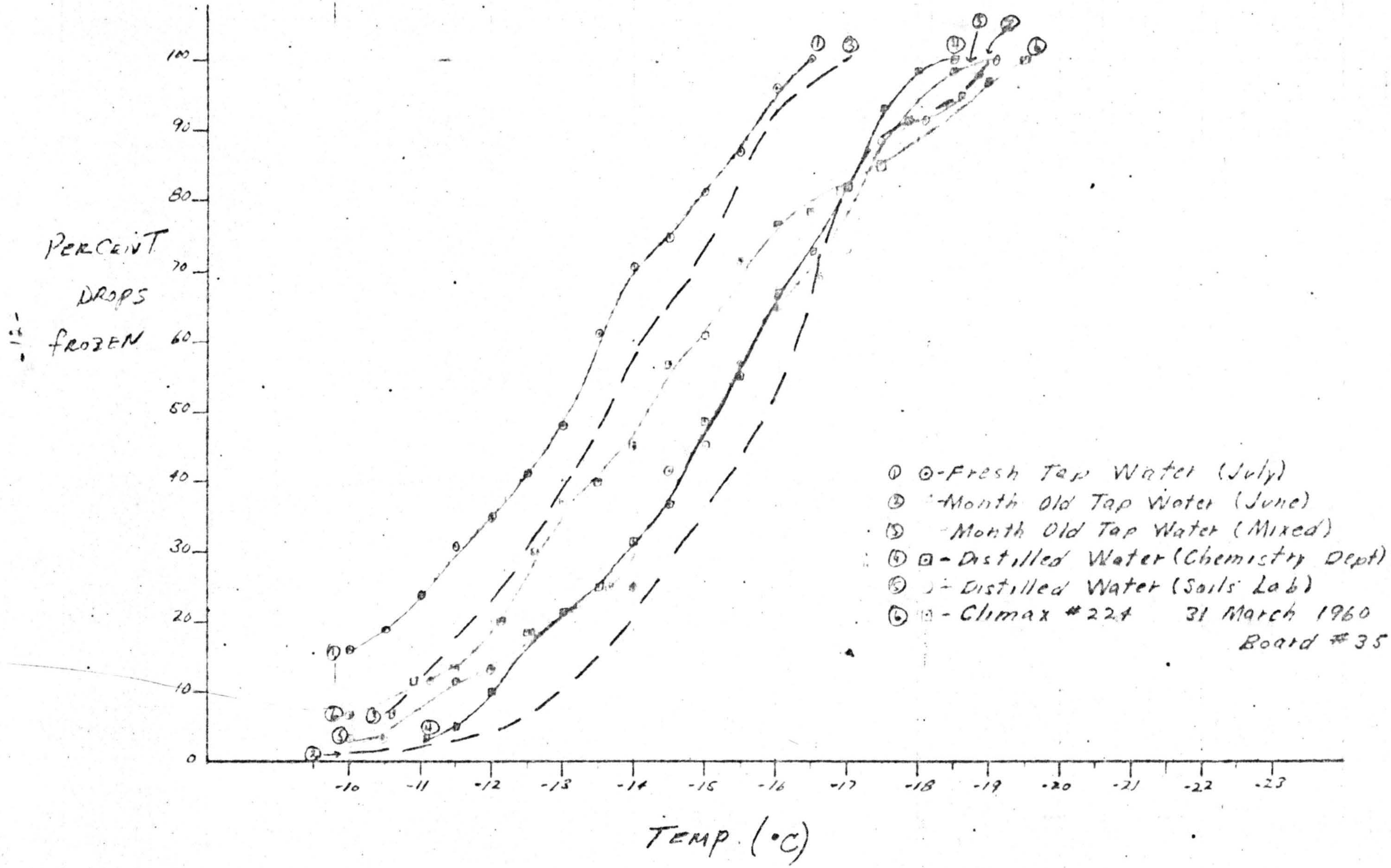
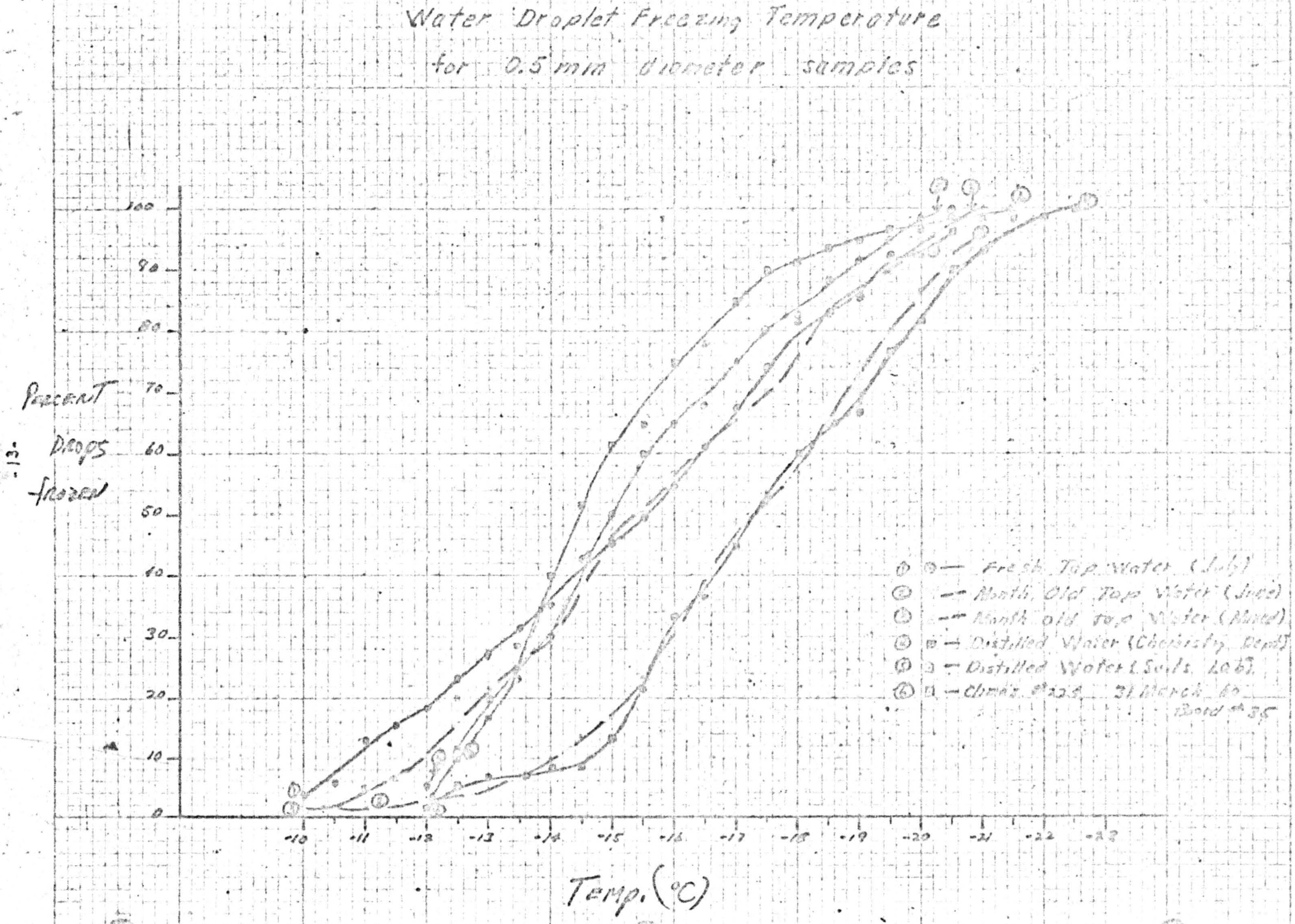
Water Droplet Freezing Temerature for 1.0 mm diameter samples.




Water Droplet Freezing Temperature
for 0.5 mm diameter samples
Percent Drops frozen
100
90
80
70
60
50
40
30
20
10
0
-10
-11
-12
-13
-14
-15
-16
-17
-18
-19
-20
-21
-22
-23
Temp. (°C)
① — Fresh Tap Water (July)
② — Month Old Tap Water (June)
③ — Month old Tap Water (Mixed)
④ — Distilled Water (Chemistry Dept)
⑤ — Distilled Water (Soils Lab)
⑥ — Chem. #225 31 March 60 Bond #35

V. DISCUSSION

The method of freezing drops as it now stands has some merit. The setup can give a fairly good indication of the impurities in a water sample relative to other samples tested. The system, however, has some drawbacks. The first is that the process is rather tedious and time consuming. Second, the rate of cooling changes from day to day and hour to hour and is dependent on ambient room temperature. This rate of cooling variation will affect the freezing temperature of the drops. Third, the time that a sample has been in the unfrozen state will affect the freezing temperature. (This was not learned until Dr. Schleusener returned from Europe in early September. Consequently, none of the completed samples have this factor taken into account.) This fact will make the comparison of frozen water samples with tap water and distilled water samples difficult. Fourth, only sixty drops were frozen for each size of each water sample. This limited sampling left irregularities in the plotted values when the percent of droplets frozen was plotted against temperature. If the number of drops freezing during a given increment of temperature are plotted against the temperature intervals, they should form a bell shaped probability curve. In most cases, this curve was barely recognizable or not recognizable at all.

I feel that the experience I have gained by working in the field of research this past summer has been particularly valuable. Having finished only one year of college before participating in the Undergraduate Research Program, I did not have as much technical knowledge as I would have liked to have had. However, this deficiency indicated to me very strongly the importance of the courses which I will be taking in the next few years. I had thought about entering the field of research before last summer, but I had had no direct contact with it. The opportunity given me through the National Science Foundation has greatly stimulated my interest. I have discovered the procedures of a research project by actually taking part and by observing those around me who were involved in the same type of work.

VI. APPENDIX

The calibration data for the thermistor is included. Thermistors similar to the one used can be obtained from:

Lafayette Radio - Industrial Division
100 Sixth Avenue
New York 13, New York

The designation for a suitable thermistor is:

32 Fb2 (Fig. 3) Bead-in-glass thermistor probe,
2000 ohms ± 20% at $3.00