

Purification of pivalic acid : its evaluation as a temperature standard reference material

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온도표준 기준 물질로의 개발을 위한 pivalic acid의 고순도 정제

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Abstract The suitability of pivalic acid was confirmed as a secondary temperature standard material. Triple-point cells of pivalic acid were obtained by using combined process of vacuum distillation with zone refining. A detailed description of the purification process was given. The melting curves were used as criteria for determination of purities of pivalic acid. Triple points of these cells with purity of 99.9997 % were measured to be $35.956 \pm 0.003^\circ\text{C}$ by using the melting plateau curves. Thus the triple point cells of pivalic acid appear to be able to use for the calibration of thermistor thermometers with moderate precision.

요약 Pivalic acid를 진공 증류 및 zone refining을 이용 고순도로 정제하여 온도 표준 기준 물질로의 개발 가능성을 시험하였다. melting plateau curve를 이용하여 99.9997 % 순도의 pivalic acid cell들의 삼중점을 측정된 결과 $35.956 \pm 0.003^\circ\text{C}$ 를 얻을 수 있었다. 이상의 정밀도를 갖는 pivalic acid 삼중점 cell들은 고정밀도를 요구하지 않는 일반 thermistor 온도계류의 보정으로 충분히 사용 가능한 것으로 판단된다.

1. Introduction

Thermometry, the field of measurement of temperature, is divided into primary and secondary thermometry. Primary thermometry is defined as thermometry carried out using a thermometer for which the equation of state can be written down explicitly without having to introduce unknown, temperature-dependent constants. The gas thermometer is a good example of this type. Secondary thermometers are all those that are not primary. An obvious example is a platinum resistance thermometer, the electrical resistance-temperature relationship of which, contains unknown, temperature-dependent terms that cannot, at present, be calculated from first principles. In order to calibrate such a thermometer, it must be compared with a primary thermometer, either directly or indirectly, at as many temperatures as necessary to determine the form of the unknown temperature-dependent terms. McGee [1] gives a detailed account of this and related topics.

Direct measurements of thermodynamic temperatures are very difficult to make and are imprecise. Therefore, a practical temperature scale is constructed in such a way that any temperature measurement on it is a close approximation to the numerically corresponding thermodynamic temperature. The temperature scale consists of a set of defining fixed points (DFP_s) together with specified instruments with specified equations for interpolating between them. The fixed points are based on the temperature variation of

the physical properties of substances. This variation may be continuous or discontinuous, as when a substance undergoes a first-order change of state.

The International Practical Temperature Scale (IPTS) [2,3] names thirteen defining fixed points and the collective role of which is to define the scale between 13.81 K (-259.34°C) and 1337.58 K (1064.43°C). Of the defining fixed points, four are triple points, four are freezing points, and five are temperatures at which a chosen pressure is exerted by the saturated vapor of the working substance. IPTS also mentions 33 secondary reference points (SRP_s) ranging from 13.956 to 3695 K. Cox and Vaughan [4] have stated the purpose of the secondary reference points as (i) the calibration of thermistors, wherever this cannot conveniently be done by use of the defining fixed points and interpolation procedures, and (ii) the calibration-checking of thermometers that have already been calibrated.

Out of the 33 secondary reference points, only two are based on the equilibrium states of organic materials (triple point of phenylbenzene, 26.871°C and the triple point of benzoic acid, 122.37°C). Glicksman et al [5], have provided a reason for the abundance of metals and the scarcity of organic materials as standard temperature reference materials. According to them, a close approximation to a reversible equilibrium state can be easily achieved in metals which crystallize in simple centro-symmetric crystal structures, in contrast to organic materials. The difficulty in obtaining and maintaining sufficiently

pure organic materials has been stated as one of the reasons for this behavior. However, with the advent of purification techniques such as zone melting, organic materials can be purified to very high levels of purity. It is for these reasons that we consider here the development of pivalic acid (PVA; $(\text{CH}_3)_3\text{CCOOH}$) as a temperature standard reference material.

It can be easily seen that among the DFPs and SRPs there are only 5 points in the range of -10°C to 100°C , in which a considerable amount of precision thermometry work is conducted. Out of these, the freezing point of sodium and the boiling point of water are difficult to realize in practice, leaving essentially three different temperatures, the triple point of water, triple point of phenoxybenzene and the triple point of gallium, at 0.01, 26.871 and 29.772°C , respectively. It is fairly easy to obtain triple point of water cells but cells of phenoxybenzene are not easily obtainable. Though gallium cells are readily available, they have their own disadvantages. They are cumbersome and relatively expensive. The cells must be made of a flexible material to allow for the expansion of gallium on melting in order to avoid the danger of breakage.

Mangum [6] and Mangum and El-Sabban [7] have thoroughly verified the suitability of succinonitrile (SCN) as a temperature reference standard near 58.08°C . Since at least three points are required for the calibration of any thermistor thermometers, pivalic acid with a melting point of around 36°C can be used in conjunction with SCN and

triple point of water cells to provide a fairly evenly spaced range for the calibration of thermistors. It is also remarkable that the melting point of PVA is very close to the temperature at which most biochemical reactions are carried out and also to the human body temperature. This makes PVA as ideal candidate for the calibration-checking of thermistors used in bio-chemical and bio-medical research, since fixed points at temperature values close to which specific tests are conducted are more convenient and accurate than arbitrary fixed points.

PVA has already been purified to high and consistent levels of purities in our laboratory [8-10]. Its thermo-physical quantities are also measured with reasonable accuracy to permit relating melting behavior with purity of the sample [10]. In addition, it is relatively cheap and non-toxic. The purpose of present study is to prepare pivalic acid triple-point cells with different purities by using vacuum distillation and zone refining. Consequently, its suitability as a standard temperature reference material is investigated by means of the melting plateau tests.

2. Determination of purity of the material

The majority of triple-point cells used have highly purified working substances within them. The equilibrium temperature of a particular sample must be close to the melting point of pure material in order to have good inter-cell reproducibility of tem-

perature and also to reduce the dependence of the equilibrium temperature on the fraction frozen.

Smit [11] gives the equation relating the concentration of the impurities and the depression of the solid-liquid equilibrium as :

$$T_F = T' - \frac{X}{FA} \quad (1)$$

where T_F is the equilibrium temperature of the actual sample when the mass fraction of the charge that is liquid is F ; T' is the melting point of a completely pure sample; X is the mole fraction of all liquid soluble impurities in the batch of working substance; A is known as the cryoscopic constant and is given by $\frac{\Delta H}{RT'^2}$, where ΔH is the latent heat of fusion and R is the gas constant. The assumptions made in the derivation of the above equation are : (i) the concentration of impurities is very small *i.e.*, it is a dilute solution, (ii) the liquidus and solidus are straight lines, (iii) thermodynamic equilibrium exists during the freezing and melting processes, and (iv) the contaminants are totally miscible in the liquid phase and totally immiscible in the solid phase.

An important criterion of the quality of a triple-point cell is the change in equilibrium temperature when F varies between certain limits. Cox and Vaughan [4] have suggested $F=0.75$ and $F=0.25$ as realistic limits within which thermodynamic equilibrium ought to be attainable for all working substances. They also assumed that the equilibrium temperature of a triple-point cell should not fall by more than 1 mK when changes from 0.75 to 0.25. Using Eq. (1) they arrived at a qual-

ity criterion which gives the maximum permissible value for X as a function of the cryoscopic constant $X=3.75 \times 10^{-4}A$. Therefore it is possible to estimate the maximum permissible impurity content for any working substance the cryoscopic constant for which is known.

A modified form of Eq. (1) can be used to obtain more realistic estimates of X , where the assumption that the impurities are insoluble in the solid phase is not used. This equation has been given by Cox and Vaughan [4] as :

$$T' - T_F = \frac{X}{A} \left[\frac{1}{F + \left(\frac{k}{1-k}\right)} \right] \quad (2)$$

Here k is the distribution coefficient, and for non-zero values of k , this equation admits the possibility that impurities may dissolve in the solid phase.

The calculated values of X , the maximum permissible impurity content for various substances, using both equations has been listed in Table 1. It is evident from the Table 1 that the impurity content must be in the ppm range in order to ensure the 1 mK criterion. The purity requirement is more stringent for metals than for organic materials. However, SCN and PVA show a significant deviation from organic materials like n-Icosane. This is due to the anomalously low values for ΔH for SCN and PVA compared to most organic compounds.

Equation (1) can be modified to eliminate the equilibrium temperature of the pure substance T' . The resulting equation can be written as :

Table 1
The calculated values of X using equations (1) and (2)

Working substance	A (K ⁻¹)	Maximum possible value of X(10 ⁶)	
		Using Eq.(1)	Using Eq.(2)
Argon	0.0294	11	29
Carbon dioxide	0.0222	8.3	22
Water	0.00972	3.7	9.7
Mercury	0.00503	1.9	5.0
Gallium	0.0073	2.7	7.3
Indium	0.00212	0.79	2.1
Zinc	0.00184	0.69	1.9
Cyclopentane	0.0023	0.86	2.3
Methylcyclopentane	0.0488	18	49
Benzene	0.0152	5.7	15
Phenoxybenzene	0.0230	8.6	23
1,3-Dioxlan-2-one	0.0165	6.2	16
n-Butanol	0.0331	12	33
n-Icosane	0.081	30	81
Succinonitrile	0.00432	1.62	4.3
Pivalic Acid	0.0028	1.05	2.8

$$X = \frac{A(T_{F1} - T_{F2})}{\left[\frac{1}{F_2} - \frac{1}{F_1}\right]} \quad (3)$$

Since it is difficult to measure the solid or liquid fractions at any point during a melting process, Mangum and El-Sabban [7] have modified Eq. (3) to include the ratio of time elapsed to the total time taken for melting instead of fraction frozen. The time fractions can be calculated by knowing roughly when the plateau starts and when it ends. The assumption is that, for the melting experiment, the material starts to melt at the beginning of the plateau and all of it melted at the end of the plateau. When one refers to the plateau, one should know that it is not

perfectly flat but has a small slope. One can obtain a flat temperature profile only if the material is perfectly pure. Therefore, Mangum and El-Sabban [7] justified that the temperature difference between the bath and the working material is essentially constant during the progression of a melting plateau and hence the rate absorption of heat by the sample is relatively constant during melting. Consequently, the fraction of sample melted can be considered to be directly proportional to the time elapsed during the melting. Hence Eq. (3) becomes modified to

$$X = \frac{A(T_{t1} - T_{t2})}{\left[\frac{1}{t_1} - \frac{1}{t_2}\right]} \quad (4)$$

where F_1 and F_2 have been replaced by the ratios of time elapsed to total time taken for melting t_1 and t_2 , respectively. The purity of the PVA samples prepared in the present experiments is calculated by using Eq. (4). Time fractions of 0.1 and 0.5 for calculation because Mangum established that this range gives the most accurate purity estimates.

3. Experimental

3.1. Purification of the material

Pivalic acid of 99.9 % purity (Sigma Chemical Co.) was further purified by series of three successive vacuum distillations followed by a variable number of zone refining stages. Zone refining requires that feed material be sufficiently pure for maximum efficiency. Since most organic materials are not stable at high temperature and may decompose before the normal boiling point is reached, vacuum distillation was performed which reduces the operating temperature to safe levels.

3.1.1. Vacuum distillation

Vacuum distillation system used is commercially available reflux type (Reliance Glass Works Co., Model R3005). It consists mainly of a reboiler, packed column, reflux controller, condenser and a vacuum pump with two cold traps. The column is equipped with a silvered vacuum-jacket to prevent heat loss. Packing material used is spring type stainless steel of size $3 \times 3 \times 1.5$ mm.

The reboiler (three-neck round flask, 5000ml) with 600 W heating mantle was filled with about 3500 ml of as-received pivalic acid. Another flask of the same type served as a receiver. The temperature controller of the heating mantle was set to around $75 \sim 80^\circ\text{C}$. Cooling water at temperature of $30 \sim 33^\circ\text{C}$ was circulated through the cooling coil of the condenser by using a thermostat. A complete distillation run takes about 14 hours and about 70 % of the original material is distilled over.

After the first distillation, the PVA left in the reboiler is discarded and the material in the receiving flask acts as the feed for the second distillation. Once the second distillation was completed, the cleaned manifold as shown in Fig. 1 was connected to the nozzle of the distilled column. This acts as the receiver for the third and final distillation. The manifold offers the convenience of holding the materials under vacuum during the purification step. The manifold was assembled using the individual components: a 500 ml flask with two necks, 28 mm tubing of sufficient length, three triple point-cells and a vacuum port.

About 450 ml of material is collected in the flask of the manifold. Then, the manifold

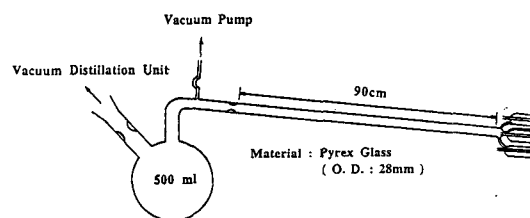


Fig. 1. Schematic diagram of the manifold with triple-point cells

is sealed off constriction A under vacuum. Note that the whole system remains under vacuum through this process. A series of melting and freezing steps are applied to the manifold as a degassing process and then most of the PVA is transferred from the flask into the zone refining tube, not directly but by means of evaporation and condensation. This might be considered as a fourth distillation. The manifold is then sealed off constriction B hermetically, allowing zone refining tube with the triple point cells at one end to be separated from the flask and the vacuum port. The material in the tube is then ready to undergo subsequently zone refining.

3.1.2. Zone refining

The tubes filled with PVA are placed inside the columns of heaters and connected to the lifting chains by means of pre-fabricated hooks. The triple-point cells are now at the top and there is empty space needed to allow the expansion of PVA upon melting and to facilitate subsequent rinsing of the triple-point cells. The currents of heaters provide the optimum heat necessary to melt the PVA and to maintain the least possible zone length. In this experiment, a zone length of about 2 cm and an inter-zone spacing of about 8 cm was realized. Detailed description on zone refining system is given elsewhere [12].

The timer of the pulling motors in the zone refining system was adjusted so that it takes approximately 24 hours for the tubes to be pulled up to the top and stop the

motor. This period is referred to as one stage of zone refining. After the end of each stage, the tubes are lowered manually, and the next zone refining stage is started. After 5 stages, a small amount of PVA at the top of the tubes was molten, and the triple-point cells were rinsed. The purpose of the rinsing with PVA is to remove the trace impurities, if any and permit them to pass through the zone refining process. After a few days, a growing cloudiness was found as the impurities concentrated at the bottom of the tubes.

After the desired level of purification (desired number of stages) was achieved (5, 10, 15 or 20 stages), the tubes were removed, and the PVA was molten and the triple-point cells filled. The filling was done sequentially, one cell receiving the top most material and, hence, the purest PVA, and the next cell receiving the middle material, and so on. In any case, not more than the top 60 % of PVA was transferred. Each cell holds approximately 60 grams of pivalic acid.

The triple-point cell of PVA is a cylindrical Pyrex glass container with an entrant tube which serves as a thermometer well. The outside diameter and the length of the outer glass shell are 35 mm and 120 mm, respectively. Thermometer well is constructed of uniform bore tubing of 5 mm inside diameter and 190 mm length.

3.2. Realization of the triple-point of the PVA cells

A thermostat used is filled with an 80-20

mixture of ethylene glycol and water and insulated on all sides and the top using 2-inch Styrofoam sheets. The bath has both a heating and a cooling system, and the temperature is controlled by their combined effect. The cooling was obtained by passing water through the cooling coil placed inside the bath using a constant temperature circulator (Haake, Model D8-L). The heating was obtained by an immersion type electric heater which is controlled by a Proportional-Integral precision temperature controller (Tronac, Model PTC-41). The controller uses a Tronac thermistor probe, placed close to the triple-point cell, to sense the bath temperature. A stirrer is used in order to achieve uniformity of temperature within the bath. From this assembly, the temperature of the bath can be maintained stable within ± 0.2 mK for long periods of time.

The temperature of the bath was measured using a standard platinum resistance thermometer (SPRT; Chino Works, No. RS53 A-5) in conjunction with an automatic A.C. precision resistance thermometer bridge (Tinsley Co.). Its temperature repeatability is less than ± 1 mK, and the drift rate when used at temperatures less than 630°C is circa 1 mK/year. The Tinsley bridge is self balancing and reads directly in ohms with a maximum reading of 159.999,99 ohm, a resolution of 10 micro-ohms, and a maximum deviation from linearity of ± 1 ppm. The current through the thermometer is 1 mA at 435 Hz. A built-in IEEE-488 interface makes it easy to transmit the resistance reading to a computer of rapid calculation

of temperature and for storage and analysis of data.

The thermometer used for measurement of the temperature of the triple-point cell was a standard platinum RTD, which was inserted into the thermo-well of the triple-point cell. The resistance of the RTD can be read using the same bridge, and the computer program modified to record both the temperature and the cell temperature at pre-set constant intervals of time. This arrangement has the advantage of using a platinum RTD instead of a thermistor the resistance of which would be much higher (in the $k\Omega$ range) and hence could not have been measured using the A.C. bridge.

Typical experimental procedure was illustrated in Fig. 2. The PVA in the cell was completely melted by placing the cell in a water bath at about 40°C . Then the cell was removed and a cold copper rod inserted into

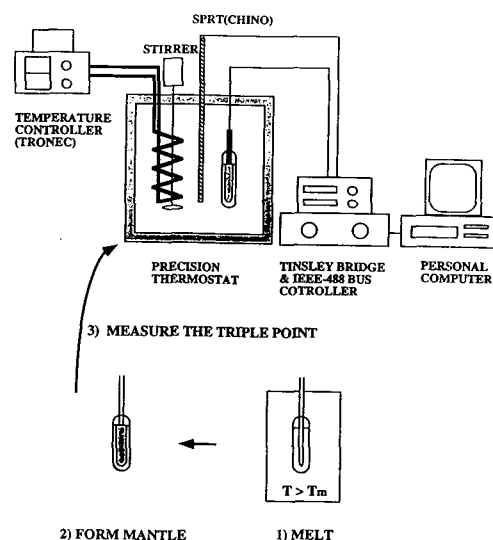


Fig. 2. Schematic diagram of typical experimental procedure

the thermometer well of the cell. The rod was removed when a layer of solid PVA had formed around the wall of the thermo-well. Melting experiments were performed by placing the PVA cell, containing the platinum RTD in the thermometer well in the constant temperature bath. Then the temperatures were recorded as the PVA melted until there was no more solid left in the cell. A light mineral oil was used as the heat transfer medium inside the thermo-well.

4. Results and discussion

All of the melting experiments were performed with the bath at 36.25°C or 36.5°C. There was no appreciable difference in the quality of the melting plateau recorded, except for the shorter duration of the plateau at higher bath temperatures. Hence, the value of the bath temperature is trivial, as long as a plateau lasting a considerable duration of time is produced at that temperature.

Figure 3 represents typical melting curves with different levels of purity (See Table 2). The increase in the range of temperatures over which the material melts (or the decrease in sharpness of the plateau) is rather obvious as we look at the melting behavior of the samples that have undergone fewer and fewer stages of purification. Figure 3 (A) shows the variation of solid/liquid equilibrium temperature of PVA, which was purified with one stage of vacuum distillation. However, it can not be found any plateau in

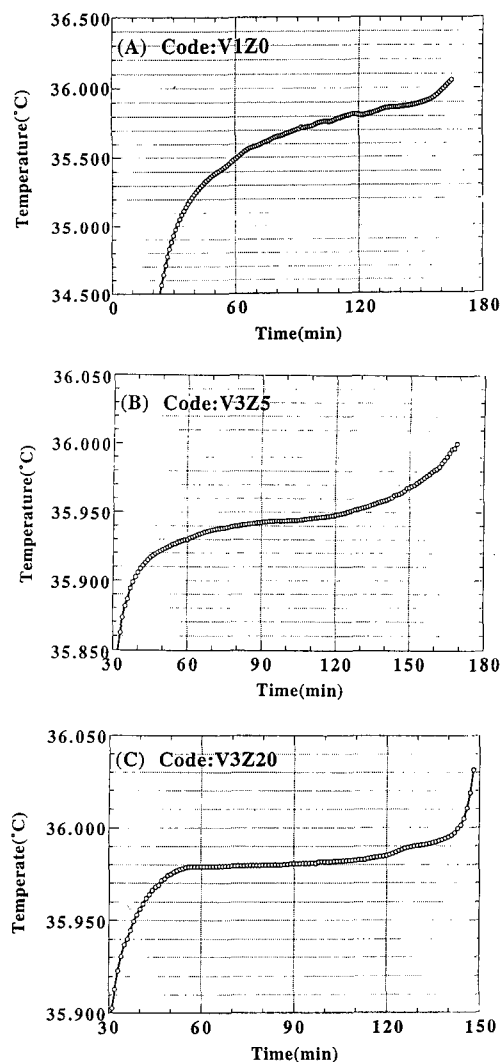


Fig. 3. Melting curves of pivalic acid at various levels of purity

melting temperature that may indicate representative equilibrium state of solid/liquid at the given level of purity. It only shows that melting point increases monotonously in the range of temperature 35.4 to 35.8°C as PVA is melted continuously. As portion of melt of PVA increases, impurities are incorporated continuously and equilibrium tem-

perature also changes subsequently. Therefore it is difficult to define the equilibrium temperature of the PVA with the purity of about 99.98 %.

Figure 3(B) represents a equilibrium temperature of PVA that was vacuum-distilled three times followed by zone refining five times. In this Figure, equilibrium temperature is shown to be at about 35.940°C, which suggests the level of purity is much improved. Indeed, the purity of this sample was approximated to be 99.9993 %. Finally, it was obtained that triple point cells of PVA with its purity level of 99.9997 %, as shown in Fig. 3(C). Here material used is even for the purest material, the melting plateaus were not perfect and a curvature was found usually at the beginning of the run. This might be due to the low thermal conductivity of pivalic acid. The equilibrium triple point of the purest PVA samples studied

was obtained to be 35.958 ± 0.003 K. This uncertainty in the value of the triple point is acceptable if the cell is going to be used for the calibration of thermistors of moderate precision.

The impurity content of the samples was estimated by application of Eq.(4) to the melting (temperature vs. time) data. These time fractions used in the calculation were typically 0.1 and 0.5 as recommended by Mangum and El-Sabban [7]. It must be noted that the purities calculated are just estimates and are not absolute. There is a certain amount of uncertainty involved in delineating the start and end of the melting plateaus, especially so at relatively low purities. There is also an uncertainty in the value of the cryoscopic constant used. This can however be eliminated by considering the ratio of the impurity contents of two samples rather than their absolute values. The resu-

Table 2
Estimates of the purity of triple-point cells of pivalic acid

Level of purification	Code* of cell	No. of applied Vac. distillation	Purification process zone refining	Estimate of purity (%)
0**	V0Z0	0	0	99.900
1	V1Z0	1	0	99.980
2	V2Z0	2	0	99.989
3	V3Z0	3	0	99.997
4	V3Z5	3	5	99.9993
5	V3Z10	3	10	99.9996
6	V3Z15	3	15	99.9997
7	V3Z20	3	20	99.9997

*V_xZ_{xx} : V and Z indicate Vacuum distillation and Zone refining and numbers indicate number of stage of vacuum distillation and zone refining applied, respectively.

**As-Purchased.

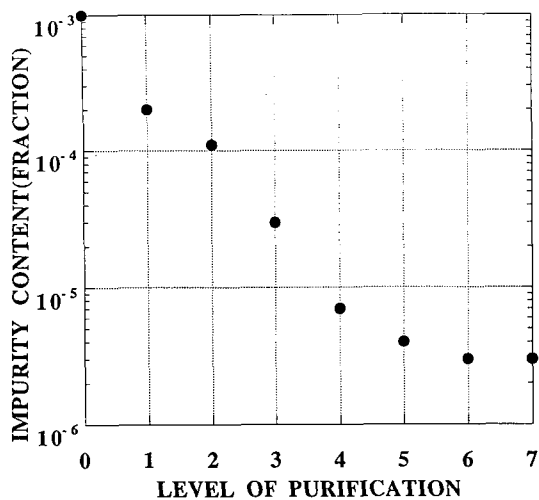


Fig. 4. Impurity content versus level of purification

Its are tabulated in Table 2.

The same results are shown in a semi-logarithmic plot of the impurity content in fraction against the level of purification if Fig. 4. A curve passing through the points would have two distinct region : a initial region of steadily declining impurity content and a final region of almost constant impurity content. It can easily be seen that there is no appreciable amount of purification after 10-15 stages of zone refining, which is equivalent to approximately 30-45 passes. This strongly suggests that a practical ultimate distribution has already been achieved after only ten stages of zone refining.

5. Conclusions

Triple point cells of pivalic acid as a temperature standard reference material were developed. Their level of purity were approx-

imated to be 99.9997 % and triple point of pivalic acid cells was measured to be $35.956 \pm 0.003^\circ\text{C}$. In this level of temperature stability, the cells can be used for the calibration of thermistors of moderate precision.

For confirmation in the performance and standardization of the triple point cells of pivalic acid, improvement in purity level of 99.9999 % or higher is required as succinonitrile triple-point cells which have been developed previously in our laboratory. However, for improvement in the purity of pivalic acid, more sophisticated techniques seem to be required prior to zone refining. The obvious way to increase the purity of the final product is to have a purer material as feed for the zone refining process. It is known that there is a substantial amount of water present in the pivalic acid raw material [13]. This water may be removed by azeotropic distillation of the raw material with benzene, as described by Brissaud et al [14]. Any residual benzene may subsequently be removed by the usual series of vacuum distillations. This procedure might ensure a better feed for the zone refining step and hence a better final product.

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