

## **AUTOMATED PLATINUM RESISTANCE THERMOMETER FOR DETERMINING THE COMPOSITION OF SALT SOLUTIONS AND PURITY OF TNT**

J.M.C. RIDDEN

*C-I-L Inc., Explosives Research Laboratory, McMasterville, Quebec  
J3G 1T9 (Canada)*

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### **Summary**

This communication describes the use of an electronic instrument to aid in the determination of the composition of certain aqueous oxidizer salt solutions, and also its application to determining the purity of trinitrotoluene (TNT). The instrument consists of a platinum resistance thermometer coupled with a bridge circuit which monitors small temperature changes.

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### **Introduction**

In the manufacture of water-gel explosives, the oxidizing components frequently consist of ammonium and sodium (or calcium) nitrates and water. These ingredients are often prepared as a hot aqueous bulk solution which is incorporated with fuels or sensitizing components (such as TNT). For the safe and efficient transportation, storage and effective performance of this type of explosive the composition of the salt solution and the purity of the TNT must be maintained.

To determine the composition of a three-component solution, two measurements are required. In the case of a mixture of ammonium nitrate (AN), sodium nitrate (SN) and water, determination of the specific gravity and crystallizing point (the so called "fudge-point") of the hot liquor can be carried out. By inspection of a chart the composition of the liquor can be obtained.

The determination of the purity of 2,4,6-trinitrotoluene is commonly monitored by the solidification point (also referred to as the "set-point") [1] in manufacturing plants. The temperature rise following the cooling of a stirred liquid sample reaches a maximum depending on the level of impurities in the TNT. The maximum defines the solidification point.

Alternative methods to determine the purity of TNT utilize gas liquid chromatography (GLC) [2] which can be used to measure the amounts of mononitrotoluene and dinitrotoluene (DNT) isomers and the unsymmetrical

TNT isomers. High performance liquid chromatography (HPLC) can be used to determine products of nitration which have significantly higher melting points than TNT, for example hexanitrobenzyl [3]. The solidification point for a particular TNT sample can be predicted from the chromatographic analysis using the expression:

$$\text{Solidification Point} = 80.65 - T$$

where  $T$  = sum of percentage impurities multiplied by individual factors. The factors for DNT and TNT unsymmetrical isomers are 0.632 and 0.507, respectively.

The Clausius-Clapeyron equation can be used to calculate the depression of freezing point of 2,4,6-trinitrotoluene due to the presence of unsymmetrical isomers. For every 1% of isomers, the solidification point will be lowered by  $0.5^{\circ}\text{C}$ .

Although the above instrumental techniques are capable of determining the impurities in TNT, the standard acceptance test for this explosive remains the solidification point.

Crystallizing points or solidification points are typically measured with a mercury-in-glass thermometer. In the case of aqueous liquors described above, the thermometer has sub-divisions of  $0.1^{\circ}\text{C}$ ; for TNT solidification

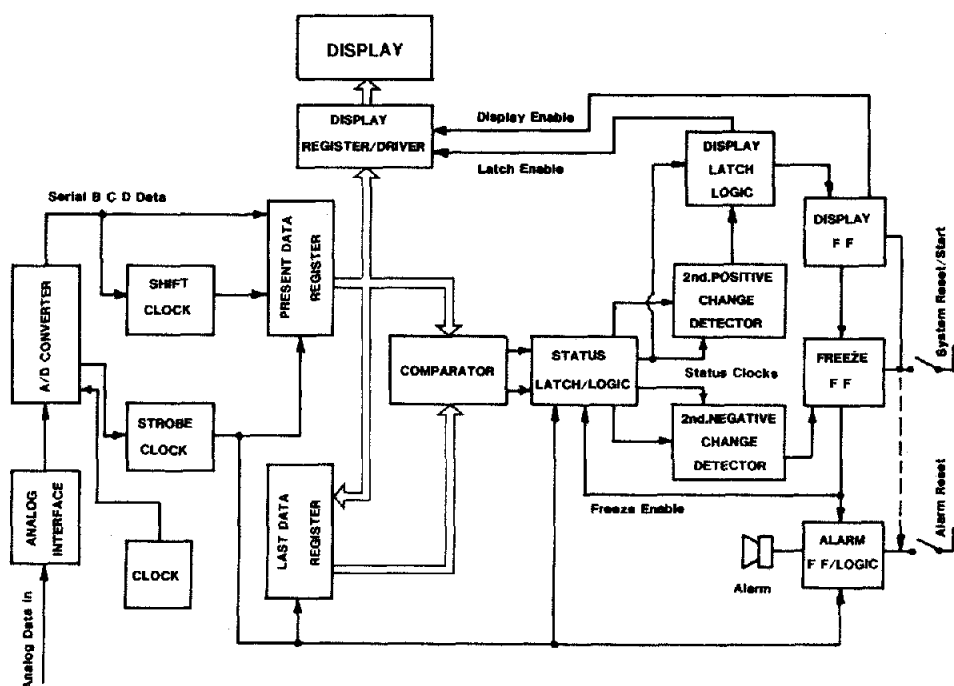


Fig. 1. Block diagram of the instrument.

point determinations the thermometer has sub-divisions of  $0.05^{\circ}\text{C}$ , and readings are estimated to  $0.01^{\circ}\text{C}$ .

Mercury-in-glass thermometers are fragile, sometimes difficult to read and hard to automate for production purposes. An electronic system was therefore designed which uses a platinum resistance thermometer coupled to an electronic circuit which senses the maximum temperature and dis-

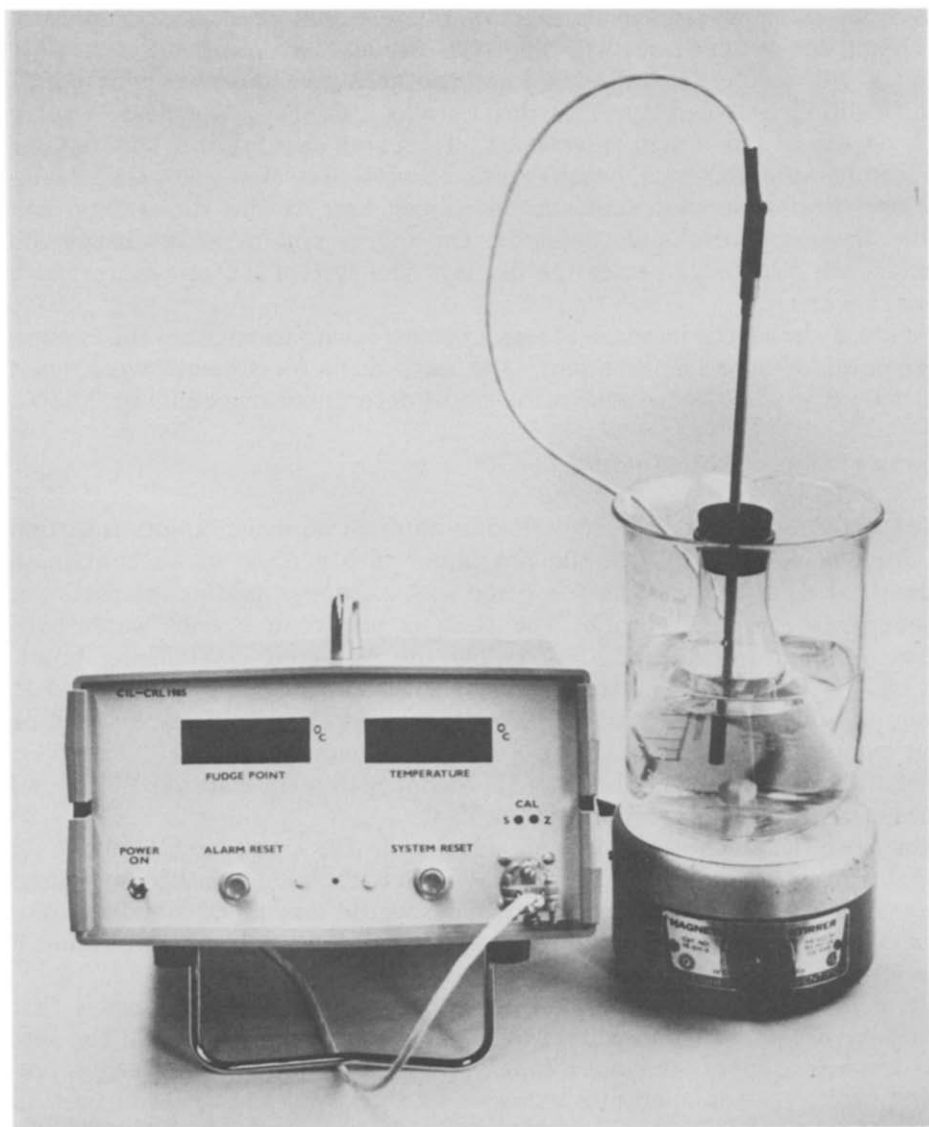


Fig. 2. Instrument and equipment set up to determine the crystallizing point.

plays the result in large numerals. A block diagram is shown in Fig. 1. The following is a brief description of Fig. 1.

The circuit has two separate systems; the digital electronic thermometer and the detector. The thermometer is a temperature-dependent platinum resistance probe of 500  $\Omega$  RTD. The probe is interfaced with a precision 4.5 digit single-chip analog-to-digital converter. The change in resistance due to temperature changes is converted into binary-coded decimal data and displayed.

The crystallizing point/solidification point circuit functions as follows: Activating the system reset will blank the display. Two positive temperature changes will enable display latch logic and activate the crystallizing point/solidification point display. This display will trail the temperature display by 1 degree as per design interaction of present data register, last register and comparator. When a negative transition is detected (i.e., slight temperature drop following a maximum as per Fig. 4) the status logic will enable the negative change detector. On the second negative change the counters are disabled, freezing the display. The system is then reset prior to the next reading.

Figure 2 shows the instrument and a typical set-up to measure the crystallizing point of an aqueous liquor. The instrument for aqueous work reads to 0.1°C, that for TNT solidification point determinations reads to 0.01°C.

#### Experimental procedure (in brief)

The determination of the crystallizing point of aqueous liquors is carried out by placing a sample of the hot liquor into a flask which contains a magnetic stirring bar. The flask is fitted with a stopper holding the platinum resistance thermometer probe. The flask is placed in a cool water bath whose temperature is about 8°C below the expected crystallizing point. The bath is placed on a magnetic stirrer. The stirred solution cools and at the point where crystals start to form the temperature will rise. Depending upon conditions and concentration, this temperature rise will be about 0.5–1.0°C for a typical solution (AN at 65; SN at 15; water at 20% w/w) whose crystallizing point will be about 45°C.

The specific gravity of the hot solution is measured at 5°C above its crystallizing point using a hydrometer. With a chart which has been prepared by measuring the crystallizing point and specific gravity of standard solutions, the composition of the unknown liquor can be determined. Figure 3 shows a portion of the chart.

To determine the solidification point of TNT, the solid sample is first melted in a test tube, then allowed to cool with stirring while the test tube is suspended in air. The temperature drop is monitored using a pre-heated probe. The temperature increases to a maximum at the solidification point before again falling.

When the above temperature changes are monitored with the electronic

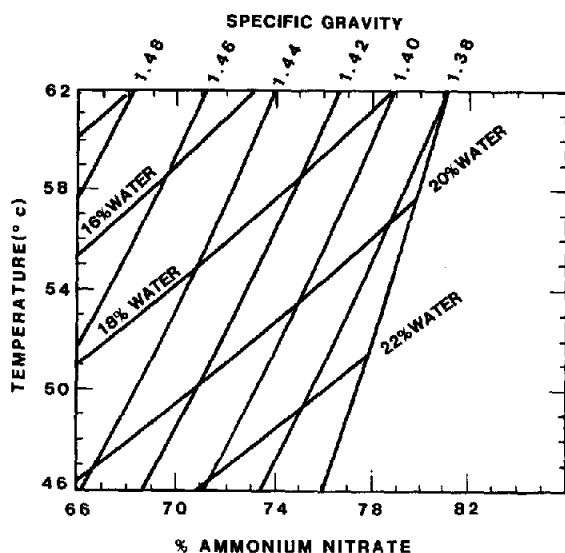


Fig. 3. Portion of the chart relating composition to crystallizing point and specific gravity. *Reading the chart:* If crystallizing point and S.G. were measured and found to be 53.5 and 1.40, respectively, then composition would be 75% AN; 20% water and 5% SN (by difference).

instrument, the maximum temperature reached is “frozen” on the display panel. An auxiliary display panel continues to monitor temperature changes so that the instrument can also be used as a regular digital thermometer.

## Results

Table 1 shows a typical temperature-versus-time reading for an aqueous oxidizer solution of AN/SN/water obtained using a mercury-in-glass thermometer and the instrument. Figure 4 is a plot of the instrument’s response which illustrates the temperature spike occurring during cooling. The instrumental precision ( $0.2^{\circ}\text{C}$ ) is adequate for production purposes. Readings can be made to agree with the glass thermometer by adjusting the electrical compensator in the instrument.

Table 2 shows the results following a series of determinations of the solidification point of commercially produced TNT, carried out on different days using the same sample. The result is compared with the value obtained with a carefully standardized mercury-in-glass thermometer. The positive correction obtained with the instrument can either be subtracted from further determinations on production samples or compensated for electronically so that the instrument displays the corrected value. Periodic instrument checks using a mercury-in-glass thermometer are carried out.

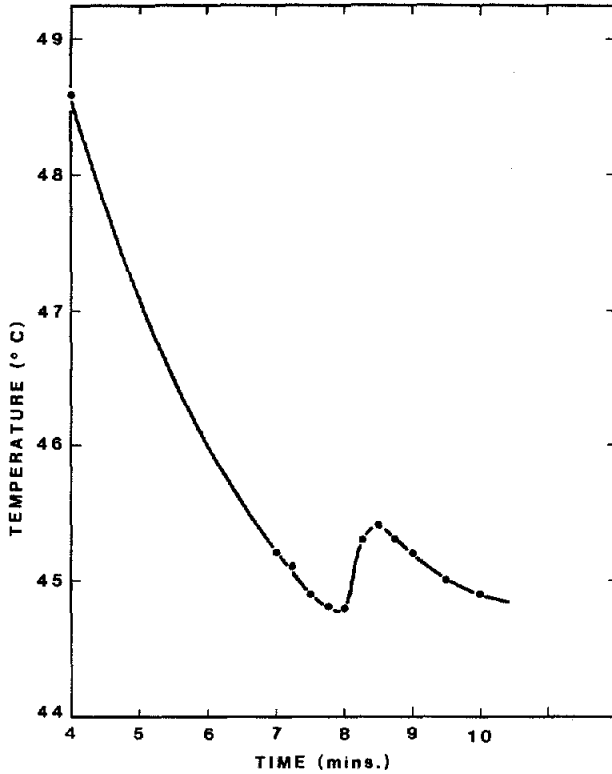


Fig. 4. Cooling curve showing temperature rise and maximum.

TABLE 1

Temperature changes during cooling of an AN/SN/water solution: mercury-in-glass thermometer versus instrument

Cooling time (min)	Temperature °C	
	glass thermometer	instrument
4	48.6	48.6
7	45.1	45.2
7¼	44.9	45.1
7½	44.7	44.9
7¾	44.6	44.8
8	44.5	44.8
8¼	45.0	45.3
8½	45.2 <sup>a</sup>	45.4 <sup>a</sup>
8¾	45.1	45.3
9	45.0	45.2
9½	44.8	45.0
10	44.7	44.9

<sup>a</sup>Crystallizing point.

TABLE 2

Set-point of TNT using the instrument, compared with a mercury-in-glass thermometer

Day	1st Test	2nd Test	Average	Difference <sup>a</sup>
1	80.45	80.42	80.44	+0.07
2	80.44	80.45	80.45	+0.08
3	80.46	80.39 <sup>b</sup>	80.46	+0.09
4	80.46	80.46	80.46	+0.09
5	80.46	80.46	80.46	+0.09
6	80.46	80.46	80.46	+0.09
7	80.46	80.46	80.46	+0.09
Overall average			80.46	+0.09
Actual value using glass thermometer			80.37	

<sup>a</sup>From glass thermometer.<sup>b</sup>Rejected on statistical basis (*t*-test for outliers) and experience which indicated that the probe was not sufficiently pre-heated.

## Conclusions

The electronic instrument can determine, with similar precision to a mercury-in-glass thermometer, the solidification point of TNT and the crystallizing point of certain aqueous salt solutions. It has the added advantage of being easy to use and minimizes operator attention. It can be automated; for example, a printer can be added, or a control to stop the stirring of TNT prior to recording the solidification point. There are no glass parts to break.

For TNT solidification point work the metal stirrer should be covered with a plastic sleeve to minimize the likelihood of metal-metal contact between the stirrer and probe.

This instrument has not been used to determine solidification points of other explosives or mixtures. It might be useful, for example, for work with DNT, or Pentolite compositions.

## Acknowledgement

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## References

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