

Determination of the Melting Point of Methyl-3-Nitrobenzoate Samples and potential OME
Applications.

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I. Abstract

The melting points of four methyl-3-nitrobenzoate samples previously synthesised and recrystallised from hot ethanol were determined using a Cole-Parmer M200 melting-point microscope. Each sample (A–D) was measured twice, giving eight determinations in total and allowing mean melting points to be calculated. The nominal melting point of methyl-3-nitrobenzoate is approximately 78 °C. Samples A–C displayed mean melting points between 75.0 and 77.0 °C, whereas sample D melted at 72.0 °C. Visual inspection under the microscope showed a clear correlation between crystal appearance and melting behaviour. Samples with white, well-formed crystals gave higher melting points, while a yellow, clumped and strongly odorous sample gave the lowest value. The data was interpreted in terms of impurity levels remaining after the earlier nitration and recrystallisation steps. The experiment demonstrated that melting-point determination provides a rapid, low-cost method for comparing the purity of organic intermediates relevant to energetic-materials manufacture.

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1. Purpose

The purpose of the experiment was to determine the melting points of four methyl-3-nitrobenzoate samples (A–D) and to use these measurements to evaluate their relative purity by comparison with the nominal melting point.

2. Hypothesis

Based on the recrystallisation procedure used [1] (Cranfield Nitration process in appendix A), it was expected that:

- Each sample would melt over a narrow temperature range close to the material Nominal value of 78 °C for methyl-3-nitrobenzoate.
- Samples containing fewer impurities would exhibit higher melting points and narrower ranges, while more impure samples would display depressed and possibly broadened melting points [2].
- Samples with whiter, less clumped crystals would appear purer and therefore would melt nearer to the Nominal value than more yellow or clumped samples.

3. Variables

3.1.Independent variables:

- Identity of methyl-3-nitrobenzoate sample (A, B, C, D).
- Trial number for each sample (first or second determination).

3.2. Dependent variables

- Melting point recorded for each trial ($^{\circ}\text{C}$).
- Mean melting point calculated for each sample.
- Qualitative appearance of each sample (colour, clumping, crystal habit, odour).

3.3. Controlled variables

- Type of melting-point apparatus (Cole-Parmer M200 microscope).
- Heating rate during the ramp (approximately $2\text{ }^{\circ}\text{C min}^{-1}$).
- Capillary tube type and approximate fill height.
- Number of measurements per sample (two runs, giving eight runs in total).
- General laboratory conditions and safety measures.

4. Theory

The melting point of a solid is the temperature at which the solid and liquid phases exist in equilibrium. For organic compounds, the melting point is widely used as a simple test of identity and purity. Pure solids normally melt sharply within a few degrees of the accepted nominal value, whereas the presence of impurities usually leads to a lower melting temperature and a broader melting range. This effect arises because foreign molecules disrupt the regular crystal lattice and reduce the lattice enthalpy; the solid therefore requires less thermal energy to melt [3].

In the earlier nitration practical, methyl benzoate was nitrated and the product methyl-3-nitrobenzoate was recrystallised from hot ethanol [3]. During recrystallisation, the impure

solid was dissolved in hot solvent, the solution was cooled slowly, and crystals were allowed to form. Impurities remained preferentially in the parent solution. After filtration and washing, no methyl benzoate was expected to remain in the product [2].

Reliable melting-point data is important in ordnance, munitions and explosives (OME) because they support the quality control of energetic compounds and their precursors [4]. Well-defined melting points help to confirm that stable, reproducible materials are being handled, which is essential when intermediates may eventually be incorporated into energetic formulations [5].

5. Observations & Data

5.1. Nominal Data

The nominal melting point of methyl-3-nitrobenzoate was identified as $78\text{ }^{\circ}\text{C} \pm 2\text{ }^{\circ}\text{C}$ [6]. Methyl benzoate was noted to melt at about $-12\text{ }^{\circ}\text{C}$ [7], confirming that any residual methyl benzoate would act as a liquid impurity rather than as a separate crystalline phase at the temperatures studied [8].

5.2. Experimental Data

Each of the four samples A–D was examined under the microscope, and the melting point was measured twice. Table 1 shows the collected results.

Sample	Appearance under Microscope	Trial 1 °C	Trial 2 °C	Mean °C
A	Slightly yellow, fine crystals, glossy white overall	75	75	75.0
B	Slightly yellow, some clumping, glossy white	76	77	76.5
C	White, glossy crystals, minimal clumping	77	77	77.0
D	Yellow, clumped, heavy odour, flat poorly defined crystals	72	72	72.0

Table 1 – Sample Data

5.3. Calculations

For each sample, the mean melting point $\bar{T}$ was calculated from the two measurements:

$$\bar{T} = \frac{T_1 + T_2}{2}$$

For example, for sample B:

$$\bar{T}_B = \frac{76 + 77}{2} = 76.5\text{ °C}$$

Deviations from the central nominal value of 78 °C were then considered qualitatively (A: –3.0 °C; B: –1.5 °C; C: –1.0 °C; D: –6.0 °C).

6. Results and Discussion

The experimental results show that all four samples melted at temperatures at or below the nominal value, as expected when trace impurities are present. However, substantial differences between samples were observed. Samples below are ordered by expected purity.

Sample C displayed the highest mean melting point, 77.0 °C, only 1 °C below the central nominal value. The two measurements agreed exactly, indicating excellent reproducibility. Under the microscope, the sample appeared white with glossy, well-formed crystals, and almost no clumping. These observations are consistent with a sample of relatively high purity [9], in which the earlier recrystallisation and washing steps removed most of the coloured by-products and residual solvent [1].

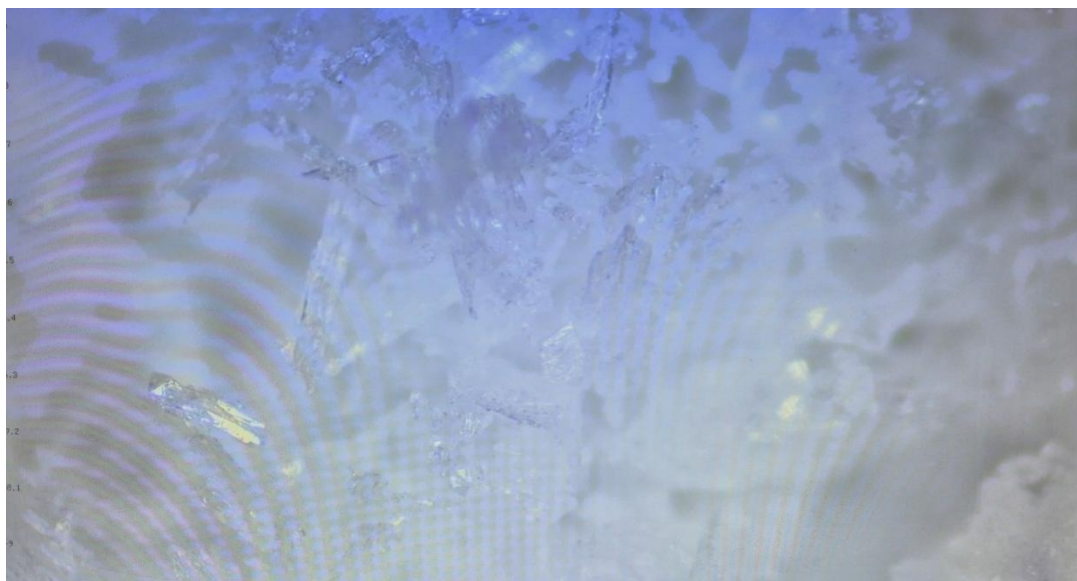


Figure 1 – Sample C Microscope view

Sample B showed a mean melting point of 76.5 °C. The small difference of 1 °C between trials lies within the typical uncertainty associated with visually observed melting points. Slight yellowing and some clumping were noted, although the crystals remained glossy. This behaviour suggests that sample B was slightly less pure than sample C but still of good quality.

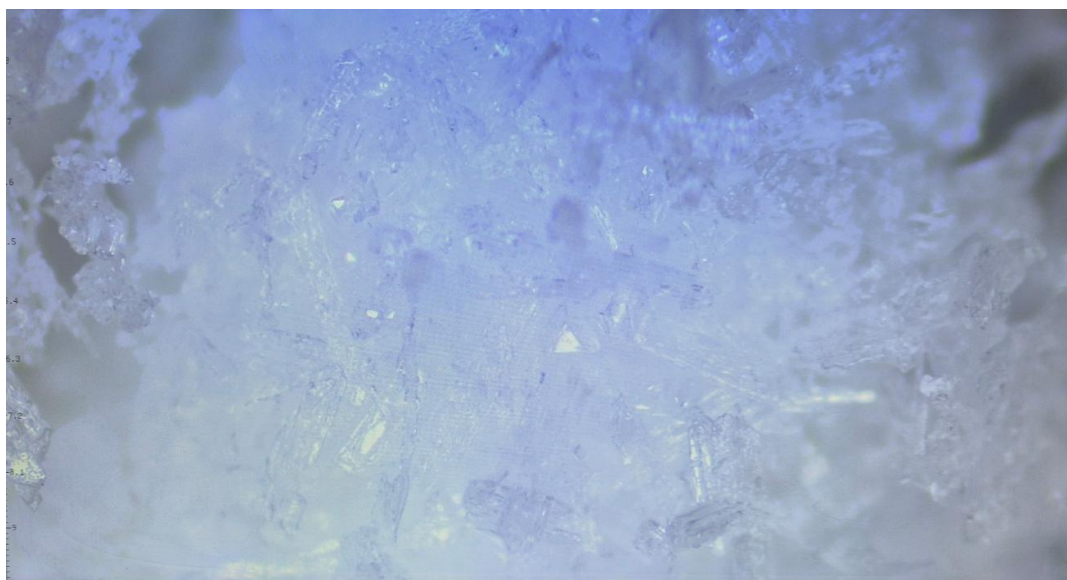


Figure 2 – Sample B Microscope view

Sample A had a mean melting point of 75.0 °C, around 3 °C below the nominal value. Again, the two trials gave identical readings, indicating that the depression arises from the composition of the sample rather than from random error. The appearance was slightly yellow but fine and glossy. The lower melting point implies a higher impurity level than in B or C, which may have resulted from less efficient recrystallisation or incomplete removal of the parent solution.

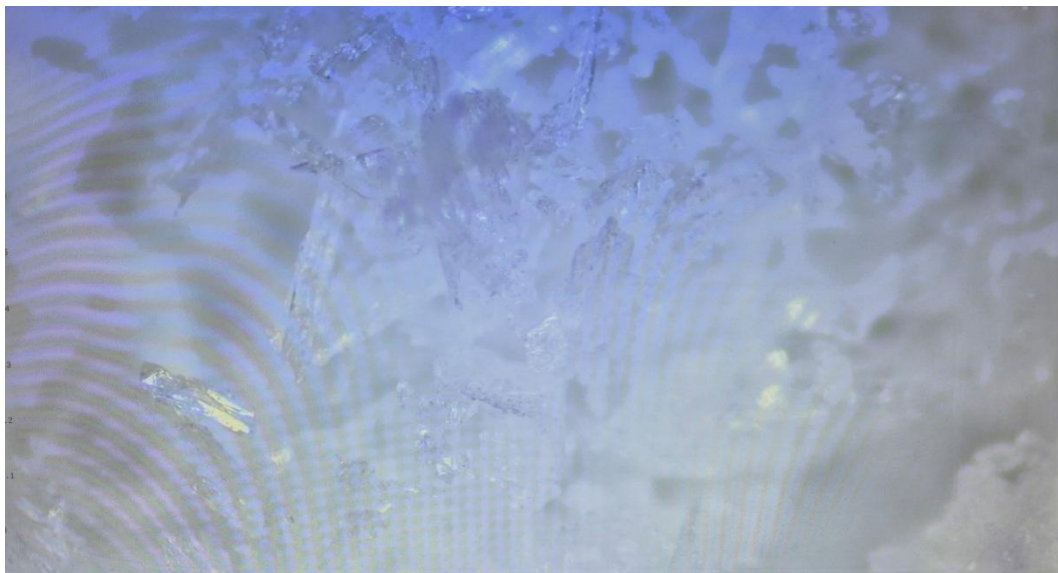


Figure 3 – Sample A Microscope view

Sample D was clearly the least pure. A mean melting point of 72.0 °C was recorded in both trials, representing a substantial depression of approximately 6 °C relative to the nominal value and lying well below the 78 °C $\pm$ 2 °C range. The sample appeared yellow and strongly clumped, with a pronounced odour and flat, poorly defined crystals. Such features are typical of material containing significant amounts of residual solvent, unreacted starting material or decomposition products [10]. The heavy odour and colour strongly suggest that volatile side-products or traces of nitrating acids remained trapped in the solid.



Figure 4 – Sample D Microscope view

Primary sources of experimental error must also be considered. Determination of melting points using a microscope relies on visual judgement of the point at which the last crystals disappear; such judgement typically introduces an uncertainty of 1–2 °C. Minor differences in the height and packing density of the sample in the capillary can lead to small variations in heat transfer and thus in apparent melting temperature [11]. Instrument calibration and thermal lag between the thermometer and the sample can also affect the recorded values, although these systematic effects would influence all samples similarly and therefore do not account for the large differences between A–C and D. The close agreement between duplicate measurements for each sample indicates that random errors were small relative to the observed differences in melting point.

7. Conclusion

The melting-point determination of four methyl-3-nitrobenzoate samples demonstrated clear differences in purity between preparations. Sample C, with a mean melting point of 77.0 °C and white, well-formed crystals, appeared to be the purest, followed by sample B, which showed a slightly lower mean melting point of 76.5 °C but still laid within the expected nominal range. Sample A, with a mean melting point of 75.0 °C, was judged to be moderately impure, while sample D, with a markedly depressed mean melting point of 72.0 °C and yellow, clumped, poorly crystalline material, was identified as the least pure.

Overall, the data supported the original hypothesis. Purer samples exhibited higher melting points closer to the nominal value and better-defined crystalline appearance, whereas more impure material was characterised by yellow coloration, clumping and significantly depressed melting points. The strong correlation between microscopic appearance and melting behaviour, together with the good repeatability between duplicate measurements, showed that melting-point determination is a sensitive and practical tool for assessing the relative purity of methyl-3-nitrobenzoate samples derived from different synthetic runs. In an OME context, this approach is therefore well suited to rapid quality control of solid precursor and intermediate materials prior to their use in further energetic-material development.

WORD COUNT $\approx$ 1125 not including Title, Abstract, Table of contents, Tables, References, Appendix.

8. References

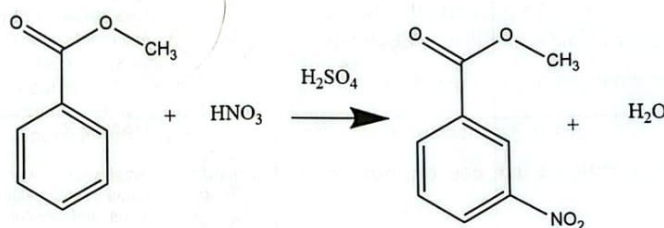
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9. Appendix A – Cranfield Nitration process

Experiment 1: Preparation of methyl-3-nitrobenzoate

Nitration is an important reaction in the manufacture of TNT, where the hydrogen atoms in a toluene molecule are replaced by nitro groups in a stepwise reaction. Benzene and benzene derivatives can undergo electrophilic substitution, where a hydrogen on the aromatic ring can be substituted with an electrophile, in this case a nitronium ion is generated by the mixed acid to produce a nitration reaction.



methyl benzoate + nitric acid $\longrightarrow$ methyl-3-nitrobenzoate + water

This reaction is very similar to that of the preparation of Di-nitrotoluene (DNT)

Hazards in the preparation of methyl -3-nitrobenzoate

All chemicals used in this experiment are harmful by inhalation, ingestion, and absorption through the skin. They must be handled in the fume cupboard and appropriate gloves worn. Nitric acid and sulfuric acid are highly corrosive and therefore very damaging to tissue. Any splashes must be washed off immediately with large amounts of water. Methyl benzoate is irritating to eyes, skin, and respiratory tract. Wash the affected areas with water. Remove to fresh air away from contaminated area for respiratory irritation. Ethanol is a potential irritant which causes drowsiness and impaired perception.

You will have been given a lab coat, safety glasses and be wearing appropriate clothing i.e., no open toes shoes or sandals. Feet covered with robust material. No shorts or skirts but legs covered to protect against possible splashes of conc. acid. Appropriate gloves can be found at the end of the bench. No eating (including chewing gum) or drinking in the laboratory. Listen carefully to the induction & follow the lab script.

Before Nitration
MB - light turquoise
MA - Clear

Reaction Procedure

ALL HANDLING OF ACIDS IS TO BE CARRIED OUT IN A FUME CUPBOARD (FC).

Label glassware appropriately throughout the practical.

1. In a recirculation fume cupboard, weight out 2.7g of methyl benzoate into a 25cm³ conical flask using a Pasteur pipette.
2. In the ducted fume cupboard, measure out 5cm³ of concentrated sulfuric acid using a 10cm³ measuring cylinder, add to the methyl benzoate.
3. Swirl the flask gently to mix and cool the mixture by placing the conical flask in ice.
4. In a separate 5cm³ conical flask, prepare the nitrating mixture. Using a 10cm³ measuring cylinder, measure 2cm³ of conc. sulfuric acid and transfer to the conical flask labelled mixed acid. — MB
5. To this add 2cm³ of concentrated nitric acid, you can use the same measuring cylinder to measure both acids. — MA
6. Cool the mixed acids to 5°C by placing the conical flask in ice.

Turn the water bath on. During the nitration process make a note of any colour changes.

7. When the methyl benzoate mixture reaches 5°C add the nitrating mixture drop by drop to the solution of methyl benzoate using a pipette, ensuring the nitrating mixture does not get into the rubber teat.
8. Stir the mixture with a glass rod keeping the temperature below 10 °C. Allow the mixture to cool to 5 °C between additions.
9. When all the nitrating agent is added, leave the mixture to stand at room temperature for 15 minutes. This will be a very slow process for the first half of the mixed acid addition which will take ~1hr (due to the exothermic nature of the reaction) until equilibration when addition generates a lot less heat and addition is much faster.
10. During the 15-minute waiting period weigh out ~25g of crushed ice and place in a 100cm³ beaker.
11. Pour the reaction mixture from the conical flask onto the ice, stir until all the ice has melted and crystalline methyl-3 nitrobenzoate has formed.

Recrystallisation Procedure

12. Move the filtration equipment from your bench into the ducted fume cupboard. Fit the Buchner funnel into a Buchner flask and clamp it to prevent it falling over. Place the filter paper in the Buchner funnel and damp with a little chilled, distilled water. Connect the flask to the vacuum line with the tubing supplied.
13. Gently open the vacuum, pour the contents of the beaker into the filter funnel. Wash the crystals thoroughly with cold distilled water and remove excess water using the vacuum on high for 5 minutes.
14. Transfer the crystals to a 50 cm³ beaker.
15. Place 15 cm³ of ethanol into a small conical flask stand on the hot water bath to warm the ethanol to 50°C.

Label	Identity	GHS Hazard Symbols
Methyl benzoate	$C_6H_5COOCH_3$ (l)	 WARNING H302 Harmful if swallowed.  H361d Suspected of damaging the unborn child.
Conc. Sulphuric acid	H_2SO_4 (aq)	 DANGER H314 Causes severe skin burns, and eye damage.
Conc. Nitric acid	HNO_3 (aq)	 DANGER H314 Causes severe skin burns, and eye irritation.  H290 May intensify fire.  H331 Toxic if inhaled.
Ethanol	C_2H_5OH (l)	 DANGER H225 Highly flammable liquid and vapour  H319 Causes serious eye irritation.
Methyl-3-nitrobenzoate	$(NO_2)C_6H_4COOCH_3$ (s)	 WARNING Currently Pure methyl -3 - nitrobenzoate is not classified as hazardous. If contaminated with methyl benzoate then Harmful if swallowed. May cause skin irritation and serious eye irritation. Suspected of damaging unborn child.

16. Place the beaker containing the sample on the water bath and pour small portions of the hot ethanol onto the crystals, stirring with a clean glass rod until the sample just dissolves.
17. Remove the beaker from the water bath and place onto a white ceramic tile. Leave the solution to cool to room temperature then immerse the beaker in ice water to allow the crystals of pure methyl nitrobenzoate to form.
18. Place the used Buchner funnel & flask at the back of the fume cupboard. Set up a clean Buchner funnel and flask, with a clean filter paper in the funnel. Damp the filter paper with a small portion of ethanol before turning on the vacuum. Filter the product under vacuum, dry the product by leaving the vacuum on for a few minutes. Transfer the product into a labelled, weighed sample bottle.

Give the sample to a technician who will dry it in a vacuum desiccator over lunchtime. After lunch reweigh bottle and contents to calculate amount of product obtained. Carry out melting point investigation.

Disposal of materials

Spent acid from the nitration step must be placed at the back of the ducted FC for a technician to dispose of.

Residual solvent from the purification step must be decanted into the waste solvent residue bottle supplied.

Methyl-3- nitrobenzoate to be handed to a technician, for drying in the vacuum desiccator.

Questions

1. Had toluene been used as the starting material what are the three likely products?

~~2, 3, 4 Nitrobenzene~~
2, 3, 4 Nitrobenzenes

2. Why keep the nitration mixture cool?

To stop run off reaction (controlling the reaction)