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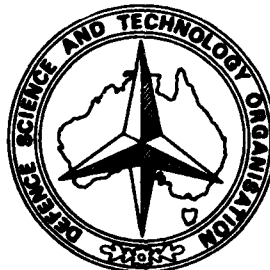
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PREPARATION AND PROPERTIES OF METHYLAMMONIUM PERCHLORATE

R.M. KEMPSON

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R.M. Kempson

S U M M A R Y

Methylammonium perchlorate has been characterized to assess its suitability as an ingredient for propellants and explosives. Details of its preparation and of methods for determining its purity are described. Its thermal stability was investigated by differential thermal analysis and thermogravimetric analysis. Its sensitivity to impact, friction, flash and flame were determined. The solubility, pH, hygroscopicity and infrared spectra were also examined.

A literature survey of its uses as an ingredient in explosives and propellants is included.

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 Methylammonium perchlorate has been characterized to assess its suitability as an ingredient for propellants and explosives. Details of its preparation and of methods for determining its purity are described. Its thermal stability was investigated by differential thermal analysis and thermogravimetric analysis. Its sensitivity to impact, friction, flash and flame were determined. The solubility, pH, hygroscopicity and infrared spectra were also examined.

A literature survey of its uses as an ingredient in explosives and propellants is included.

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1. INTRODUCTION

A large variety of organic perchlorates have been described in the literature (ref.1,2). Numerous amine perchlorates have been prepared which are generally crystalline salts and not particularly hygroscopic. They can be regarded as being derived from ammonium perchlorate (AP) by substitution of hydrogen atoms by organic groups. Hofmann et al(ref.3,4,5) prepared a number of them including the mono, di, tri, and tetramethylammonium perchlorates and measured their solubilities. Methylammonium perchlorate (MAP), which is the mono-derivative, has also been called methylamine perchlorate, aminomethane perchlorate, and methanamine perchlorate.

There is an increase in sensitivity upon replacement of a hydrogen atom in AP by a methyl group. The Trauzl lead block test value of MAP has been reported as 160% that of TNT(ref.6) and as 470 cm³(ref.7). For a charge density of 1.68 g/cm³ the detonation velocity has been reported by Roth(ref.8) as 7 540 m/s and by Ivanov et al(ref.7) as 7 630 m/s. For comparison, Roth's values for picric acid and tetryl were 7 504 and 7 665 m/s respectively. The sensitivity of MAP has been described as similar to that of lead azide(ref.6).

Since 1921 at least five patents have taken out on the uses of the methylammonium perchlorates in explosives(ref.9,10,11,12,13). Other patents have described their uses in composite propellants(ref.14) and on means of raising the decomposition temperatures of both the perchlorates and the propellants made from them(ref.15). During the last few years a number of combustion studies have been carried out on them by Russian authors(ref.16,17,18,19). MAP was included in most of the above patents and studies and the literature survey is described in Appendix 1. Of particular interest in the field of composite propellants was that their burning rates can be considerably increased by substitution of AP by MAP because MAP burns about ten times faster than AP.

This report describes further work on MAP synthesis, the results of tests used to determine the purity of MAP, and the results of tests conducted to indicate safety requirements for its use and handling.

2. PREPARATION AND PURITY

2.1 Preparation

The preparation of MAP has been effected by the neutralization of aqueous perchloric acid with aqueous methylamine(ref.7,16,17,20,21,22,23,24), by the neutralization of an alcoholic solution of methylamine with aqueous perchloric acid(ref.25), by bubbling methylamine gas into 70% perchloric acid(ref.26) and by bubbling methylamine gas into perchloric acid in ethanol(ref.27). MAP has also been prepared by reacting methylammonium chloride and other methylammonium salts with perchloric acid(ref.18,28,29). In all cases only brief details of the preparations were given but it appears that MAP was recovered by removal of water or ethanol and then recrystallized from a solvent, sometimes not identified.

The preparation of MAP was tried by several methods: aqueous methylamine was added to 71% perchloric acid, aqueous methylamine was added to 71% perchloric acid in ethanol and methylamine gas (produced by heating methylamine solution) was bubbled into 71% perchloric acid. The use of bottled methylamine gas, such as that available from the Matheson Co., would be convenient but this was not available.

The safest and most convenient method was found to be the slow addition of aqueous methylamine (Ajax L.R. Grade, 24% mass/volume) to perchloric acid (J.T. Baker Analysed Reagent, 71% mass/mass). A detailed description of the method is given in Appendix II and 37 g of MAP were obtained after one recrystallization from ethanol. The low yield of 28% was because of the high solubility of MAP in water and ethanol. The MAP could also be recrystallized from 2-propanol and from ethanol/chloroform (1:1).

All testing of MAP in this report was on a sample which had been recrystallized twice from ethanol.

A literature account of an accident which occurred during the preparation of MAP is described and discussed in Appendix III.

2.2 Chloride

Silver nitrate solution was added to solutions of MAP, and to several very dilute sodium chloride solutions, which had all been acidified with dilute nitric acid. Comparison of the turbidity produced by the formation of silver chloride indicated a chloride content (as methylammonium chloride) of less than 0.01%.

2.3 Chlorate

Manganous sulphate - phosphoric acid reagent was prepared by mixing equal volumes of saturated manganous sulphate solution and syrupy phosphoric acid. MAP solutions and very dilute potassium chlorate solutions were prepared and three drops of the reagent were added to three drops of each solution in small crucibles. The crucibles were then warmed rapidly, allowed to cool and three drops of a one per cent alcoholic diphenylcarbazine solution were added to each crucible. The chlorate content (as methylammonium chlorate) was estimated to be less than 0.02%, based on comparison of the violet colouration thereby produced.

2.4 Ammonium

As methylamine solution contains a small amount of ammonia as an impurity the amount of AP present in the MAP was determined with Nessler's reagent (ref.30), which reacts only with ammonium ions to give an orange-brown product.

A series of AP and MAP solutions was prepared and four drops of Nessler's reagent were added to 80 cm³ of each solution. The most concentrated MAP solution was 2.5 g/100 cm³ and this remained perfectly clear. AP solutions below 0.48 mg/100 cm³ remained perfectly clear, but solutions above this concentration gave a gradation of orange-brown colours. Thus the MAP contained less than 0.02% AP.

2.5 Perchlorate content

2.5.1 Determined as nitron perchlorate

MAP (0.1 g) was dissolved in water (100 cm³) and ten drops of dilute sulphuric acid were added. The solution was heated nearly to boiling and nitron acetate (12 cm³ of 10% nitron in 50% acetic acid) was added. The solution was cooled and surrounded by ice for several hours. The precipitate was filtered off in a weighed sintered glass crucible and washed with four 3 cm³ amounts of cold water. The crucible was dried at 110°C for one hour and reweighed.

The perchlorate content was 75.46%, calculated by:

$$\%ClO_4 = \frac{m_1 \times 24.11}{m_2}$$

where m_1 = mass of nitron perchlorate precipitate and m_2 = mass of MAP.

2.5.2 Determined as potassium perchlorate

The method used follows that of Arndt and Nachtwey(ref.31) and relies on the insolubility of potassium perchlorate in absolute ethanol. A saturated solution of potassium acetate in absolute ethanol (15 cm³) was added to the MAP (0.5 g) dissolved in absolute ethanol (10 cm³). The mixture was warmed to near the boiling point for 15 min, cooled and then left at room temperature for one hour. The precipitate was collected on a weighed sintered glass crucible, washed with absolute ethanol, dried at 120°C for one hour and weighed.

The perchlorate content was 75.53%, calculated by:

$$\%ClO_4 = \frac{m_1 \times 71.78}{m_2}$$

where m_1 = mass of potassium perchlorate and m_2 = mass of MAP

2.6 Chlorine content

This was determined in a manner similar to that described by Schumacher (Page 113 of ref.2) for the determination of chlorine in AP. The MAP was fused with sodium carbonate in a platinum crucible by placing it in a furnace at 200°C and heating to 830°C. The chloride formed was determined by titration with standard silver nitrate solution using potassium chromate indicator. Blank determinations were carried out by the same method but with the omission of MAP.

The chlorine content was 26.89%, calculated by:

$$\frac{V \times M \times 3.545}{m}$$

where V = net volume of silver nitrate solution (cm³)

M = molarity of silver nitrate solution

and m = mass of MAP (g)

2.7 Purity

The calculated perchlorate content of MAP is 75.62%. Therefore the perchlorate content determined by the nitron perchlorate method (75.42% Section 2.5.1) indicates a purity of 99.8%, and that determined by the potassium perchlorate method (75.53%, section 2.5.2) indicates a purity of 99.9%. However, as nitron reagent is not specific for perchlorate, the former method is subject to interference from a number of other ions. The amount of chlorate has been shown to be less than 0.02% (Section 2.3), and it is unlikely that a significant amount of any other interfering ions would be present. Nevertheless, the potassium perchlorate method is to be the preferred one for the analyses of MAP samples via the perchlorate content.

The calculated chlorine content was 26.96%. Therefore the chlorine content obtained (26.89%, section 2.6) indicated a purity of 99.7%. As negligible amounts of chloride and chlorate were detected (Sections 2.2 and 2.3) there was no interference from these sources.

The amount of AP present has been shown to be less than 0.02% (Section 2.4), therefore the above results indicate that the purity of the MAP is at least 99.7%.

3. PROPERTIES OF MAP

3.1 Solubility

MAP was found to be between moderately and very soluble in water, methanol, ethanol, 2-propanol, 2-methoxyethanol, acetonitrile, dimethylformamide and dimethylsulphoxide. The solubility of MAP in water at 15°C was determined by Hofmann et al(ref.5,6) as 110 g/100 cm³ and is about six times that of AP.

MAP was found to be slightly soluble in methyl acetate, 2-butanone (MEK), 1,4-epoxybutane (THF) and 1,4-dioxane. It was only very slightly soluble in ethyl acetate, butyl acetate and acetic acid. It was insoluble in aliphatic and aromatic hydrocarbons, chlorinated hydrocarbons, diethyl ether and diisopropyl ether.

3.2 pH

A 5% solution of MAP was prepared in carbon dioxide free distilled water of pH 6.9. Similar solutions of two AP samples were prepared: B.D.H. LR Grade AP which had been recrystallized from water, and

"propellant grade" AP which did not contain any anti-caking additive. The pH values of the solutions were determined at 20°C using a Pye pH meter fitted with a glass electrode and a calomel-saturated KCl reference electrode. The pH value of the MAP solution was 5.8 and those of the AP solutions were 5.3 and 5.4 respectively. This is in agreement with the fact that methylamine is a stronger base than ammonia (i.e. the methylammonium ion acts as a weaker acid than the ammonium ion in its hydrolysis reaction).

3.3 Density

The density of the MAP was not determined but the density of MAP crystals has been reported as 1.72 ± 0.005 g/cm³ (ref.7) and the density of cast MAP has been reported as 1.68 g/cm³ (ref.6).

There is a crystallographic phase change from monoclinic to tetragonal at a little above 50°C, with apparently a quite significant decrease in density. Stammer et al (ref.20) obtained a density of 1.58 g/cm³ at 77°C by an X-ray diffraction method, and 1.56 g/cm³ at 72°C by immersion in a silicone oil.

3.4 Sensitivity tests

Except for the glancing blow test the tests performed were in accord with ERDE Safety Committee Circular No. 3, March 1966.

3.4.1 Drop mass test

A Technoproduct falling mass machine was used and for a 3 kg mass falling 33 cm there was a 50% probability of explosion. The figure of insensitiveness was thus 29 and MAP is classified as sensitive since a standard RDX (cyclotrimethylenetrinitramine) sample and picric acid are rated at 80 and 100 respectively.

Stammer et al (ref.20) tested seven compounds including MAP on a U.S. Bureau of Mines impact machine with a test of 50% fire point with a 2 kg mass. The results for AP, RDX and MAP were 100, 35 and 20 cm respectively. That is, the MAP was found to be appreciably more sensitive than RDX which agrees with the above result. Stammer's values for di-, tri-, and tetramethylammonium perchlorates were 22, 25 and 35 cm respectively, which showed that there is a slight progressive decrease in sensitivity as substitution with methyl groups increases.

Ivanov et al (ref.7) tested the impact sensitivity of MAP on K-44-11 copra with device No. 1 (as translated from the Russian). The percentage of explosions caused by a 2 kg mass falling from a height of 25 cm was 65%. This would also indicate a similar sensitivity to those obtained above.

3.4.2 Glancing blow test

MRL designed equipment was used in which standard brass and steel torpedoes fall down a 70° incline onto material lying on a steel anvil.

The minimum energy for one in ten ignitions was 8.3 joules. The broad classification into which MAP falls from this test is that it is more sensitive to friction and impact than gunpowder.

3.4.3 Sensitiveness to friction

A mild steel mallet produced 100% ignitions with both the York stone and mild steel anvils. A boxwood mallet on the York stone anvil produced 50% ignitions, as did a mild steel mallet on the aluminium bronze anvil. Other combinations gave 0% ignitions. The results are tabulated in Table 1.

COMMENT: In assigning a sensitivity classification the results from both the impact and friction sensitivity tests are taken into account. From the results obtained, MAP is classified as sensitive. This means that impact between materials harder than softwood, including all normal metals used in construction, must be avoided.

3.4.4 Temperature of ignition

A differential thermal analyzer (see Section 3.5.2) was used with a heating rate of 5°C/min and the major peak of the exotherm pattern occurred at between 336 and 339°C.

COMMENT: This is in accord with the "explosion temperature" of 338°C reported by Datta and Chatterjee(ref.32) who dropped small amounts of compounds into test tubes immersed in a bath and noted the temperature at which explosive decomposition took place.

3.4.5 Ignition by flash

The MAP failed to ignite and is therefore described as being insensitive to ignition by flash.

3.4.6 Ignition by flame

After a flame had been held to the MAP for the one minute of the test it had failed to ignite. From this test the MAP is described as being neither an explosion nor a fire risk. However, larger amounts and/or confinement of the MAP may give quite different results: a pressure increase may well cause the MAP to burn.

It should be noted that when the flame was maintained for longer than one minute the MAP melted, ignited and was consumed in an instant.

3.5 Thermal analysis

3.5.1 Differential thermal analysis

Differential thermal analysis (DTA) was studied on a Stanton Redcroft instrument model No. 673-4. A sample mass of 30 mg and a heating rate of 10°C/min were used for most experiments. Heating rates of 5 and 20°C/min were also used. Sensitivity settings for ΔT were usually 10 or 20 mV full scale deflection.

(a) Atmosphere of static air

(i) Endotherms

At all heating rates (5, 10 and 20°C/min) the first three peaks were endotherms and the spread of the peaks varied slightly with heating rate. The first and second of these endotherms, with maxima at 54 and 183°C at 10°C/min, were shown by Stammer et al(ref.20) to be the crystallographic changes, monoclinic to tetragonal, and tetragonal to cubic respectively. The third endotherm, with a maximum at 261°C, is due to the melting of the MAP.

When a sample was heated to 272°C and allowed to cool three exotherms were obtained which indicated that the crystallographic changes and the melting are all reversible. When a sample was heated to 280°C and allowed to cool the peak corresponding to the setting of

the molten MAP was very weak and broad and an extra exothermic peak appeared at a lower temperature. This change in the cooling curve was a result of the partial decomposition of the MAP at the higher temperature reached during the heating period.

In Table 2 the exotherms are compared with those reported in the literature. It can be seen that there is good agreement in all cases.

(ii) Exotherm

After the melting a very large exotherm was obtained. It usually consisted of several peaks and was due to the decomposition of the MAP. The number and relative heights of these peaks and also the total spread of the exotherm pattern varied considerably from one determination to another. The variations were not related to the ambient storage time of the MAP.

Ten determinations were done at a heating rate of $10^{\circ}\text{C}/\text{min}$. The two examples given below are the extremes of the decomposition patterns which were obtained.

Example 1 (see figure 1). The exotherm began to rise very steeply at about 291°C ; there were peaks at 320°C (large), 325°C (large), 349°C (small) and 368°C (medium); it was substantially completed at 386°C .

Example 2 (see figure 2). The exotherm began to rise very steeply at about 286°C ; there were peaks at 346°C (large), 358°C (large), 395°C (medium) and there were several side peaks; it was substantially completed at 399°C .

When a determination was done at $20^{\circ}\text{C}/\text{min}$ there was one very large peak at 336°C .

Two further samples were heated at $10^{\circ}\text{C}/\text{min}$ to 272°C and 280°C , which is in the region of the commencement of the exotherm. They were cooled to 45°C and then reheated at $10^{\circ}\text{C}/\text{min}$ up to 400°C . Although slight decomposition had already occurred during the initial heating period the exothermic patterns were within the range of samples which had not been heated.

The DTA exotherms of MAP have been reported in the literature in slightly different ways. Stammier et al (ref.20) gave the commencement of the exotherm (330°C), Nambiar et al (ref.23,24) gave the peak maximum (343°C) and Ivanov et al (ref.7) gave the ignition temperature (330°C). Apart from Nambiar's description of a separate small exotherm at 408°C (see later), these papers made no mention of the multiple peaks or of the variability observed above. However, these temperatures all fall within the observed range of exotherm patterns.

The production of a multiple peak exotherm can be explained as follows. It has been shown by Mack and Wilmot by a matrix infrared technique (ref.21) and by Guillory and King by mass spectrometry (ref.22), that MAP decomposes principally by a proton transfer reaction to methylamine and perchloric acid. This dissociation reaction, any evaporation of the dissociation products, and also any sublimation of the MAP, are all endothermic processes. However, most of the dissociation products remain in situ and their decomposition reactions and also their reactions with each

other, are all very exothermic processes. The result is that the exothermic reactions greatly outweigh the endothermic reactions to produce a multiple peak exotherm.

The high variability in the exotherm pattern is not explained as easily. Variations in the sample mass and in the heating rate appeared to be contributing factors, but the major cause lies elsewhere. As the decomposition of MAP is of an explosive nature it may be extremely sensitive to factors such as small variations in particle size or the degree of compaction. Another factor may be a high sensitivity to variations in the number of crystal imperfections. Pai Verneker and Rajeshwar(ref.33) have investigated the effect of pre-compression on the DTA and TGA of AP. The AP was compressed into pellet form under pressures ranging from 5 to 32 MPa. The pellets were then crushed and sieved to obtain the same particle size for each sample. They observed shifts and changes in the shape of the two decomposition exotherms with the changes in the pre-compression pressures. There were corresponding changes in the mass loss by both isothermal and dynamic TGA. They explained the results in terms of introduced changes in the density of dislocations in the crystals.

Nambiar et al(ref.23) observed another exotherm at 408°C. They proved that this was due to the decomposition of AP which had been formed as a decomposition product of MAP. They suggested that a small fraction of the MAP decomposes via methyl group transfer to form ammonia and methyl perchlorate, and that the ammonia then reacts with perchloric acid to form AP. This exotherm was not observed in the present work or by the other authors(ref.7,20). To test this claim a DTA determination was interrupted during decomposition. The residue was dissolved in water and a positive test was obtained for ammonium ions with Nessler's reagent. Further tests were done in which samples of MAP were heated in platinum, silica and porcelain crucibles in a furnace at temperatures between 350 and 365°C. A temperature and heating time could be found in each case in which the residue gave a faint positive test with Nessler's reagent. This confirmed that AP is formed in a small amount but that the subsequent decomposition of AP may not necessarily be detected by DTA.

(b) Atmosphere of argon

A DTA was done under an atmosphere of argon at 10°C/min and compared with the results which were obtained in air. The endothermic peaks were identical and the exothermic pattern was similar to that in figure 2. This confirms that the existence of an exothermic pattern is independent of the presence of oxygen in the atmosphere surrounding the sample. Repeat determinations would probably produce the range of patterns which were observed in air.

(c) At low pressure

When the DTA was done at a pressure of about 130 Pa (1 mm of mercury) the endotherms occurred at slightly higher temperatures (see Table 2), than at atmospheric pressure. As the changes corresponding to the endotherms should be independent of pressure these variations cannot be readily explained.

In place of the decomposition exotherm a single large endotherm was obtained: it began at 284, peaked at 328, and finished at 360°C. This reversal of the decomposition peak agrees with Nambiar et al, although these authors obtained 308°C for the peak maximum. It is possible, however, that repeated determinations would produce variable decomposition endotherms. The change to an endotherm can be explained as follows. When MAP dissociates at low pressure the resulting methylamine and perchloric acid evaporate before they have a chance to decompose or react with each other. As dissociation and evaporation are both endothermic processes a large endotherm is observed.

3.5.2 Thermogravimetric analysis

Thermogravimetric analysis (TGA) was done on a Stanton Redcroft instrument model No. TR01. A sample mass of between 22 and 24 mg and an atmosphere of static air were used.

(a) Dynamic

Dynamic TGA was done at 5°C/min. There were analogous variations in the TGA traces with those of the DTA exotherm patterns. The possible causes of these variations have already been discussed in Section 3.5.1 (a)(ii). The TGA traces could be grouped into two types: those with one region, and those with two regions, where there was a rapid and substantial loss in mass. An example of each type is described below and shown in figure 5.

Example 1: there was no measurable loss in mass up to 285°C, a 10% loss between 285 and 312°C and then a very rapid loss to 92% at 316°C. After 316°C there was only a gradual loss to 97% at 400°C.

Example 2: the trace was very similar to example 1 up to 54% mass loss at 316°C; but then it began to level out, and there was a second rapid loss from 66 to 95% in the range 353 to 390°C. After 390°C there was only a gradual loss to 97% at 450°C.

Nambiar also heated at 5°C/min and obtained a TGA trace which was similar to that of example 1. They recorded an 8% mass loss at 319°C and then a slow loss to 97.5% at 400°C.

(b) Isothermal conditions

There was no detectable mass loss after 70 min at 245°C. When a sample was held at 255°C (start of melting) for one hour there was a 5% loss in mass. These observations are in agreement with reported results: Stammer found that there was no mass loss after 90 min at 240°C but a slow loss above 255°C, and Ivanov found that the mass loss became measurable at 260°C.

3.6 Melting point

The Encyclopedia of Explosives (ref.6) gives the reported values for the melting point as 210°C and 242°C. The origin of the first is uncertain but the second was obtained by Roth (ref.8) in 1933. The only other melting point values reported are those during the last few years by DTA: they are much higher than the above, but are very similar to each other, and average 256°C (see Table 2).

A Kofler hot stage microscope provided a clear observation of how the melting point range varies with the heating rate. If a sample was heated very slowly (less than 1°C/min) the first signs of melting occurred at 225°C, although most melted beyond 245°C, and the last trace of any solid MAP disappeared at 257°C. When a sample was heated to 254°C in only seven

minutes and then heating continued at a rate of only 1°C/min, no melting occurred until 255°C and the great majority of the sample melted at 256 to 258.5°C. These observations were the same for samples which had been recrystallized one, two or three times from ethanol, and for a sample which had been stored at ambient for eleven weeks since recrystallization.

Whereas DTA and TGA did not detect any melting or decomposition before about 250°C, the above observations indicated that these changes are taking place, to a very minor degree, from about 225°C.

3.7 Hygroscopicity

MAP was carefully ground in small amounts to a fine powder in an agate pestle and mortar. Approximately 0.8 g samples were placed in thin layers (average thickness about 0.5 mm) in platinum dishes of 60 mm diameter. The dishes were placed in small desiccators over saturated salt solutions providing 54, 66, 70.4, 72.6, 75, 79.5 and 88% relative humidity (RH) at 20°C. "Propellant grade" AP which did not contain tricalcium phosphate was treated in the same way and stored at the same humidities.

The mass increases of the MAP and the AP were recorded with time.

On exposure to 55, 66, 70.4 and 72.6% RH the MAP was only very slightly hygroscopic. After 14 days at 55% RH and after 7 days at 66% RH the increases were both less than 0.02%. After 21 days at 72.6% RH the increase was 0.08%: that is, the hygroscopicity is just becoming significant.

At 75% RH MAP is deliquescent. After 7 days it had increased in mass by 28% and there was a thin layer of liquid in the dish. After 14 days the increase was 53% and all the MAP was in solution. After 16 days the increase remained constant at 56%. At 88% RH the uptake of water became even greater: after 2 days the increase in mass was 27%.

The "hygroscopic point" is therefore about 73%. The results are shown in figure 4.

The above results agree with Ivanov et al(ref.7) who obtained a "hygroscopic point" of $73 \pm 2\%$ RH at 20°C. These authors noted that very small amounts of chloride and dimethylammonium ions greatly reduce the "hygroscopic point".

AP was only slightly hygroscopic even at 88% RH. It had increased in mass by only 0.05% after 21 days at 75% RH and by 0.11% after 12 days at 88% RH.

It is worth comparing the results obtained for MAP with those reported for ammonium nitrate (AN) (pages A324-A325 of reference 6). When AN was stored in thin layers at 22.2°C the increase in mass after 2 days was 0.2% at 52% RH, 26.1% at 76% RH and 62% at 90% RH.

MAP is therefore much more hygroscopic than AP but it is not as hygroscopic as AN.

3.8 Infrared spectrum

The infrared spectrum of MAP was recorded on a Perkin Elmer 521 grating spectrophotometer as a Nujol mull (1300 to 400 cm^{-1}) and as a Fluorube mull (4000 to 1300 cm^{-1}) on potassium bromide plates. The frequencies of the absorption bands, together with band assignments and indications of the band intensities, are given in Table 3. The spectrum of MAP is shown in figure 5.

The spectrum of AP, deuterated AP and deuterated MAP were also obtained to aid with band assignments.

The frequencies and assignments reported by Ivanov et al for MAP(ref.7); by Cabana, Sandorfy and Theoret for methylammonium chloride and deuterio-methylammonium chloride(ref.34,35); and by Ross and Hezel for AP and deuterio-AP(ref.36,37), are also listed in Table 3.

The maximum of the strong broad band due to the NH_3^+ stretching mode occurs at $3\ 240\ \text{cm}^{-1}$. The band is almost symmetrical in shape and is assigned to asymmetric stretching. It has a series of submaxima on the low frequency side which is quite common for hydrogen bonded NH_3^+ ions and generally due to overtone and combination bands that have had their intensity enhanced by resonance interactions. The position of the NH_3^+ symmetrical mode is not so easily assigned, as its position is not apparent in spectra obtained using reasonably thick mulls. However a submaximum was obtained at $3\ 185\ \text{cm}^{-1}$ in the spectrum of a thin mull of partially deuterated MAP. The separation between this band and the NH_3^+ asymmetrical mode is $55\ \text{cm}^{-1}$ compared to a separation of $87\ \text{cm}^{-1}$ for the NH_3^+ stretching bands in methylammonium chloride. After deuteration the band, due to the NH_3^+ asymmetrical mode, is shifted to $2\ 438\ \text{cm}^{-1}$. Again the band is broad and has numerous submaxima on the low frequency side. The frequencies of these submaxima in most cases do not correspond to the position of the overtone or combination bands of the protonated spectrum. The frequency difference between the two ND_3^+ stretching bands in MAP and methylammonium chloride is $78\ \text{cm}^{-1}$. The NH/ND ratios of the asymmetrical and symmetrical modes of MAP and methylammonium chloride are similar; 1.33 and 1.35 for the asymmetrical modes and 1.35 and 1.36 for the symmetrical modes. Based upon these results the band at $3\ 185\ \text{cm}^{-1}$ has been assigned to the NH_3^+ symmetrical stretching mode. The evidence does not eliminate the possibility of this band being the first overtone of the NH_3^+ asymmetrical mode which occurs at $1\ 589\ \text{cm}^{-1}$ or at least being degenerate with it. Ivanov assigned three bands at $3\ 349$, $3\ 276$ and $3\ 177$ to the NH_3^+ stretching modes. These frequencies are much higher than the frequencies recorded in this investigation.

It is not known whether the differences are caused by a different method of sample preparation or a different dispersive element in the spectrometer. No attempt has been made to determine from which fundamentals arise the numerous overtones or combination bands that occur between $2\ 908$ and $1\ 843\ \text{cm}^{-1}$.

The band due to the CH_3 asymmetrical mode can be easily identified at $2\ 988\ \text{cm}^{-1}$, some $25\ \text{cm}^{-1}$ higher than the corresponding band in methylammonium chloride. The band at $2\ 900\ \text{cm}^{-1}$ has been assigned to the CH_3 symmetrical stretching mode upon the basis of it being at about the same frequency as the corresponding band in methylammonium chloride, that it is within the accepted range for a CH_3 group attached to a nitrogen atom, and that a similar band occurs at $2\ 892\ \text{cm}^{-1}$ in deuterated MAP. It is possible that the band at $2\ 900\ \text{cm}^{-1}$ could be the first overtone of the band at $1\ 450\ \text{cm}^{-1}$. Ivanov et al assigned the two CH_3 stretching modes to bands at $3\ 070$ and $2\ 954\ \text{cm}^{-1}$. The band at $3\ 070\ \text{cm}^{-1}$ is too high for a CH_3 group attached to nitrogen atom. Either the calibration of their spectrometer was in error or the band is due to an overtone or combination band. The band at $2\ 954\ \text{cm}^{-1}$ is in about the expected position. The reproduction of the spectrum in Ivanov's paper is such that it is impossible to decide whether the CH_3 stretching modes have been assigned correctly. The position of CH_3 symmetrical stretching mode would be best solved by the use of C^{13} or by deuterating the protons of the methyl group.

It may be that the intensity of this band is too weak to be observed.

The bands due to the NH_3^+ asymmetrical and symmetrical bending modes occur at $1\ 589$ and $1\ 495\ \text{cm}^{-1}$ compared to $1\ 578$ and $1\ 534\ \text{cm}^{-1}$ in methylammonium chloride. Their assignments are confirmed by deuteration. The position of the ND_3^+ asymmetrical and symmetrical modes cannot be determined and based upon the corresponding NH/ND ratios of methylammonium chloride it appears that they could be degenerate with the broad band at about $1\ 100$ or the weaker band at $1\ 164\ \text{cm}^{-1}$. Ivanov's assignment of the bands at $1\ 596$ and $1\ 499\ \text{cm}^{-1}$ are in close agreement with the findings of this investigation.

The two bands due to the CH_3 asymmetrical and symmetrical bending modes occur at 1450 and 1422 cm^{-1} . As expected, the frequencies were not shifted by deuterating the protons attached to the nitrogen atom and they are similar to the frequencies of the corresponding bands in methylammonium chloride. They also agree closely with the values quoted by Ivanov.

The band at 1254 cm^{-1} has been assigned to the NH_3^+ rocking mode. On deuteration the band is shifted to lower frequencies and it occurs at about the same frequency as the corresponding band in methylammonium chloride. It is difficult to assign the position of the ND_3^+ rocking mode. Based upon the NH/ND ratio of the mode in methylammonium chloride the ND_3^+ rocking mode should occur at about 1180 cm^{-1} . A similar band occurred at 1164 cm^{-1} in deutero-MAP. The NH/ND ratio is 1.08 compared to 1.06 for the corresponding bands in methylammonium chloride. However, it is not possible to confidently assign the band at 1164 cm^{-1} to the ND_3 rocking mode as the ND_3^+ bending mode is also expected to occur in this region.

The broad band at about 1100 cm^{-1} , that appears to be composed of two overlapping bands at 1110 and 1070 cm^{-1} , has been assigned to the triple degenerate ClO_4^- stretching modes. Ross found three bands in AP but under the condition that the spectra were recorded for this investigation only two bands were observed. The bands are not shifted by deuteration of the protons on the nitrogen atom, but the band envelope appears to be broadened on the high frequency side. Ivanov reports two bands at 1106 and 1067 cm^{-1} .

The band at 988 cm^{-1} has been assigned to the C-N stretching mode. It is shifted to 923 cm^{-1} on deuteration giving an NH/ND ratio of 1.07. Again, this is similar to the C-N stretching mode in methylammonium chloride. A second band occurs as a weak shoulder at 930 cm^{-1} . Assignment of this band to the ClO_4^- stretching mode is based upon the fact that a weak band unaffected by deuteration occurs in the spectrum of AP, and the intensity of the NH_3^+ rocking band in methylammonium chloride is greater than the ClO_4^- stretching mode of AP. Normally the band will not be observed in the spectrum of MAP as it occurs at about the same frequency of a strong band at 918 cm^{-1} . Ivanov has assigned the ClO_4^- stretching band to 920 cm^{-1} , but as this band was not observed in the normal spectrum it is believed that it was an incorrect assignment.

The CH_3 rocking band occurs as a medium broad band at 918 cm^{-1} . On deuteration, it is shifted to 738 cm^{-1} giving an NH/ND ratio of 1.24, similar to the behaviour of the band in methylammonium chloride. Although this band has been assigned to the CH_3 rocking mode it must involve the NH_3^+ rocking mode in order to give such a high NH/ND ratio.

The two bands at 628 and 620 cm^{-1} have been assigned to the triply degenerate ClO_4^- bending mode. The band shapes and positions are similar to the corresponding bands in AP.

4. CONCLUSIONS AND RECOMMENDATIONS

MAP can be easily prepared in high purity from "reagent grade" methylamine and perchloric acid. These chemicals are readily available and are relatively inexpensive. The above are important considerations in the search for new propellant ingredients.

MAP is an explosive material, but has a high melting point, high thermal stability and a high ignition temperature. It is also resistant to ignition by flash and by flame under the conditions of the tests. However, unlike AP, it is sensitive to impact and friction and falls into the class of a primary explosive. Appropriate safety equipment and facilities are therefore required for the handling of a material of this sensitivity.

DTA and TGA showed that a number of reactions take place during decomposition, and that the relative contributions from them can vary considerably from one determination to another. There is scope for further investigation in this area.

The applications of MAP in solid propellants may be restricted to some extent. There is a crystallographic change at 54°C which results in a change in density. If the propellant composition is such that cracking would occur due to the volume change of the MAP, then the temperature during manufacture and storage would need to be kept below 50°C.

MAP should not be subjected to a humidity greater than about 72% RH as it becomes hygroscopic and deliquescent. However, under normal conditions encountered in a laboratory or propellant processing plant it would be insensitive to moisture. Nevertheless, storage in well sealed containers is required to prevent caking.

If the investigation of other substituted ammonium perchlorates is required, then the experimental work described in this report, together with the literature references, will provide the basis for evaluating their suitabilities as ingredients for explosives and propellants.

5. ACKNOWLEDGEMENTS

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APPENDIX I

A LITERATURE SURVEY OF USES IN EXPLOSIVES AND PROPELLANTS

In a British patent in 1921 Lundsgaard(ref.9) covered the methylammonium perchlorates for their uses in compositions for mines, shells, mining explosives and detonators. A Belgian patent in 1938(ref.10) covered the use of MAP in an ammonium nitrate explosive. In 1972 Kluensch et al(ref.11,12,13) described the use of MAP in safety explosives in German patents. The MAP was dissolved in a glycol or in a eutectic mixture to give safety explosives of high energy and low sensitivity. An example of one of the eutectics is a mixture of ethanolamine nitrate, methylamine nitrate, urea, ammonium nitrate and MAP. The eutectics were still liquid at temperatures of -20 to -30°C.

Several Russian papers published between 1971 and 1976 have included MAP in their combustion studies. Fogel'zang et al(ref.18,19) studied the combustion of a large number of organic perchlorates and other compounds. The perchlorates were pressed into Plexiglas tubes of 4 to 7 mm diameter under pressures of 100 to 500 MPa, and burning rates were determined between 0.1 and 40 MPa. It was found that the burning rates of the methylammonium salts were all much higher than the corresponding ammonium salts. In the case of MAP its burning rate was nearly ten times greater than AP. Viktorenko et al(ref.16,17) studied the combustion of MAP alone and with the addition of catalysts by pressing into Plexiglas tubes and burning in nitrogen in a constant pressure bomb at 0.1 to 10 MPa. They noted the good pressability of MAP and that charges pressed under a pressure of 500 MPa were transparent.

In 1973 Stammler et al(ref.14) took out a U.S. patent for the use of substituted ammonium perchlorates in composite propellants. They described propellants consisting of an organic crosslinked resin binder and an organic oxidizer such as MAP. These oxidizers were used as either partial or complete replacement for conventional inorganic oxidizers such as AP or ammonium nitrate. Propellants were obtained which had higher specific impulses and burning rates. For example they describe a polyurethane propellant in which 10% of the AP was replaced by MAP: the burning rate was increased from 17.8 to 33.0 mm/s at 6.89 MPa (1 000 psi). Details of the propellant processing conditions were given.

In a U.S. patent in 1974 Depree(ref.15) increased the decomposition temperatures of AP and substituted ammonium perchlorates by the addition of various phosphate compounds. This also enabled the propellants made from them to withstand higher temperatures.

APPENDIX 11

PREPARATION : A DETAILED DESCRIPTION

In the following procedure one mole of perchloric acid (100 g) is neutralized with one mole of methylamine (31 g). The yield is 35 to 40 g of methylammonium perchlorate (MAP) after one recrystallisation.

Add 142 g (85 cm³) of 70 to 72% mass/mass aqueous perchloric acid to 50 cm³ of distilled water in a one litre beaker. Surround the beaker with ice cubes and stir the contents with a motor driven glass stirring rod. Pour about 135 cm³ of 24% mass/volume aqueous methylamine solution into a dropping funnel. If a methylamine solution of another concentration is used then this volume should be adjusted accordingly. Suspend a thermometer in the perchloric acid and when the temperature is less than 15°C commence the addition of the methylamine solution at a rate of about two drops per second. Maintain stirring and keep the temperature below 20°C. When nearly 129 cm³ have been added remove about 0.1 cm³ of the reaction mixture and test with methyl red indicator. Continue the addition and testing until the end-point has been reached. The colour change is from red to yellow. Then add about 1 cm³ of excess methylamine solution and stir for a further fifteen minutes.

Transfer the resulting MAP solution to a 500 cm³ wide neck flask with a flat flange top add boiling chips and set up for vacuum distillation. Remove excess methylamine at room temperature by connecting to a water pump. Then connect to a vacuum pump via a pressure controlling device, a dry ice trap, and an ice-cooled receiving flask. Place the flask on a water bath at 50 to 60°C and adjust the pressure so that water distils off slowly. Continue to distil off the water until the MAP commences to precipitate out in the flask. This will be when approximately 140 cm³ of water have been distilled over.

Remove the boiling chips and cool the flask overnight in a refrigerator. Filter off the MAP, wash with a small amount of ice-cold water, briefly press dry with filter papers and then recrystallize from near boiling absolute ethanol (about 220 cm³ will be required). Allow the solution to cool slowly and leave in a refrigerator overnight. Filter off the MAP and wash with a small amount of cold ethanol and then with about 100 cm³ of ether. Dry the product to a constant mass under reduced pressure over calcium sulphate in a vacuum desiccator. It is advisable to dry only a small quantity of the product initially and submit it to sensitivity tests before proceeding to dry the bulk amount.

The dried product must be handled carefully behind a safety shield and stored in a plastic jar with a push-over top.

APPENDIX III

COMMENTS ON AN ACCIDENT REPORTED IN THE LITERATURE

Kasper(ref.38) reported an explosion during the preparation of MAP by the neutralization of methylamine (100 cm³ of a 25% aqueous solution) with perchloric acid (120 cm³ of 70% aqueous acid). The reaction mixture had been left overnight at room temperature. When an attempt was made to stir in dried crystals on the upper part of the beaker an explosion occurred.

The above volumes represent 0.8 mole of methylamine and 1.4 mole of perchloric acid, which shows that a large excess of perchloric acid was used. It is therefore likely that the MAP had become extremely friction sensitive by the presence of the included perchloric acid. It is also possible that impurities present in the reagents contributed to the explosion. The methylamine was described as "the factory's own product" and the perchloric acid as "commercial grade".

The detailed preparation in Appendix I ensures that the addition of an excess of methylamine and the use of reagents of high purity.

TABLE 1. FRICTION SENSITIVITY

| Anvil | Ignitions (%)* | |
|------------------|----------------|-------------------|
| | Boxwood Mallet | Mild Steel Mallet |
| York Stone | 50 | 100 |
| Hardwood | 0 | 0 |
| Softwood | 0 | 0 |
| Mild Steel | 0 | 100 |
| Naval Brass | 0 | 0 |
| Aluminium Bronze | 0 | 50 |

* 0 ignitions out of 10 tests0%
 Up to 6 ignitions out of 10 tests50%
 More than 6 ignitions out of 10 tests . . .100%

TABLE 2. DIFFERENTIAL THERMAL ANALYSIS
PEAK TEMPERATURES (°C) (NOTE 1)

| Heating rate °C/min | Obtained | | | | Reported | | | |
|------------------------|---|---------------|---------------|--------|----------------------------|---------------|---------------|--------|
| | | | | | Ref.20 (Note 2) | Ref.7 | Ref.23,24 | |
| Atmosphere | 5 | 10 | 20 | 10 | 30 | 4 | 10 | 10 |
| Peak No. (Note 3) | Static air | Static air | Static air | Vacuum | Static air | Static air | Static air | Vacuum |
| 1 | 52(-) | 54(-) | 54(-) | 60(-) | 48(-) | 49(-) | 50(-) | 50(-) |
| 2 | 181(-) | 183(-) | 187(-) | 194(-) | 178(-) | 179(-) | 180(-) | 180(-) |
| 3 | 261(-) | 261(-) | 260(-) | 269(-) | 255(-) | 254(-) | 258(-) | 258(-) |
| 4 | Extremely variable: see section 3.5.1 and figs. 1 and 2 | | | 328(-) | 330(+) | 330(+) | 343(+) | 309(-) |
| 5 | No other peaks observed | | | | No other peaks reported | | 408(+) | 414(+) |

NOTE 1: (-) denotes endotherm and (+) denotes exotherm

NOTE 2: Ref.20 temperatures were quoted for the commencement of the peaks

NOTE 3: Peak No. 1: Crystallographic change, monoclinic \rightleftharpoons tetragonal (reversible)

Peak No. 2: Crystallographic change, tetragonal \rightleftharpoons cubic (reversible)

Peak No. 3: Melting point

Peak No. 4: Decomposition

Peak No. 5: Decomposition of AP (formed during decomposition of MAP)

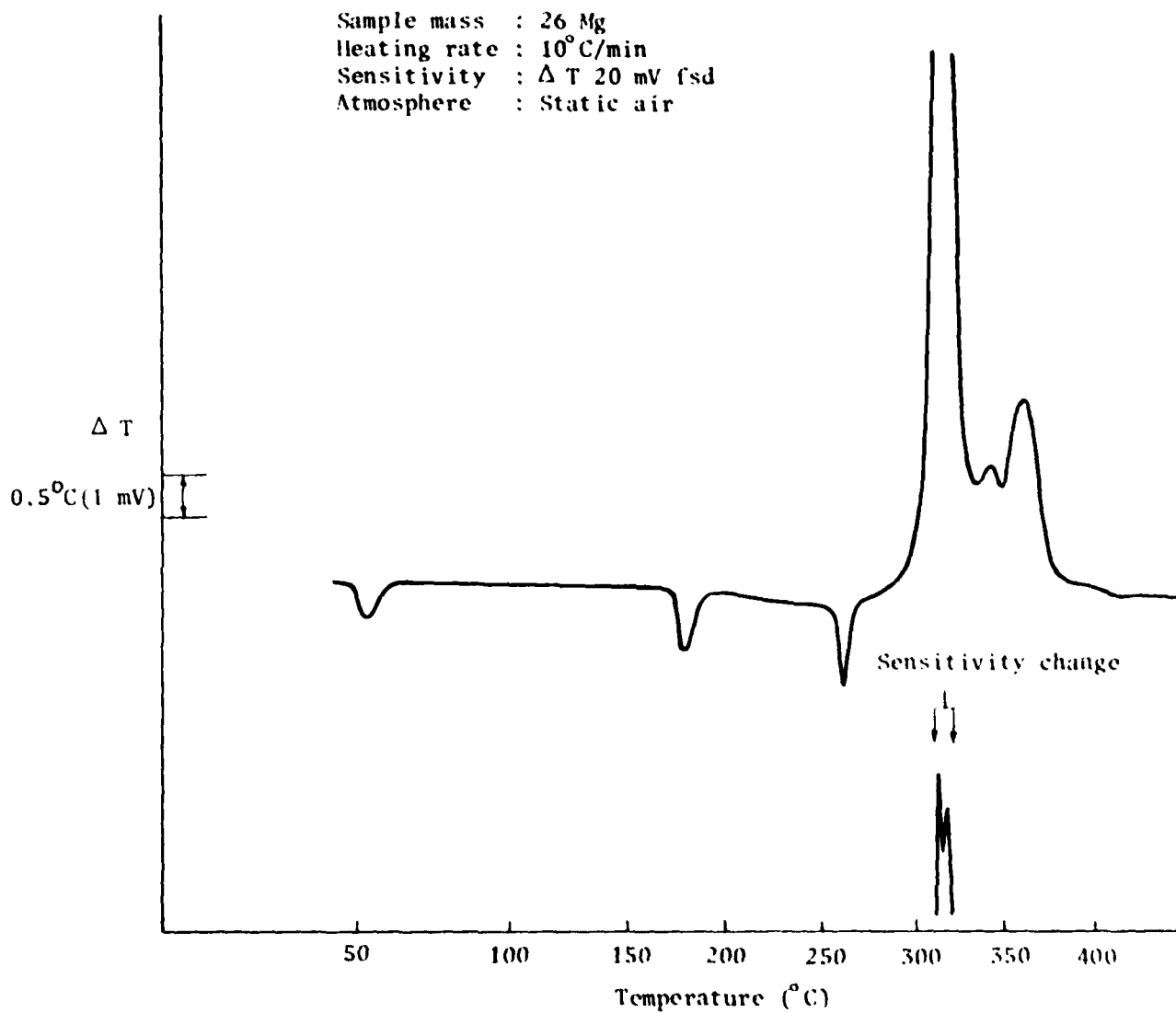


Figure 1. Differential thermal analysis : Example 1

WSRL-0016-TR
Figure 2

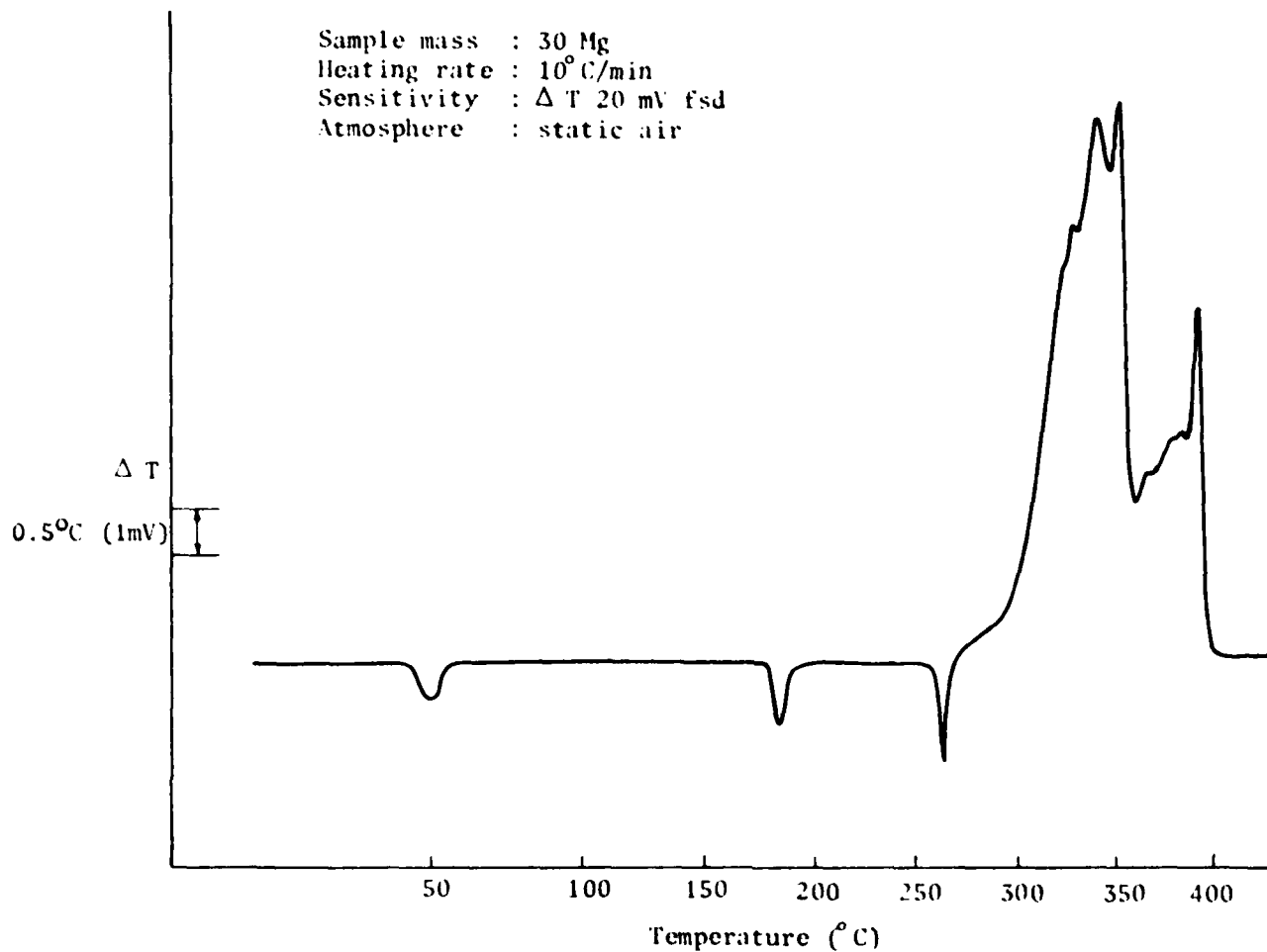


Figure 2. Differential thermal analysis : Example 2

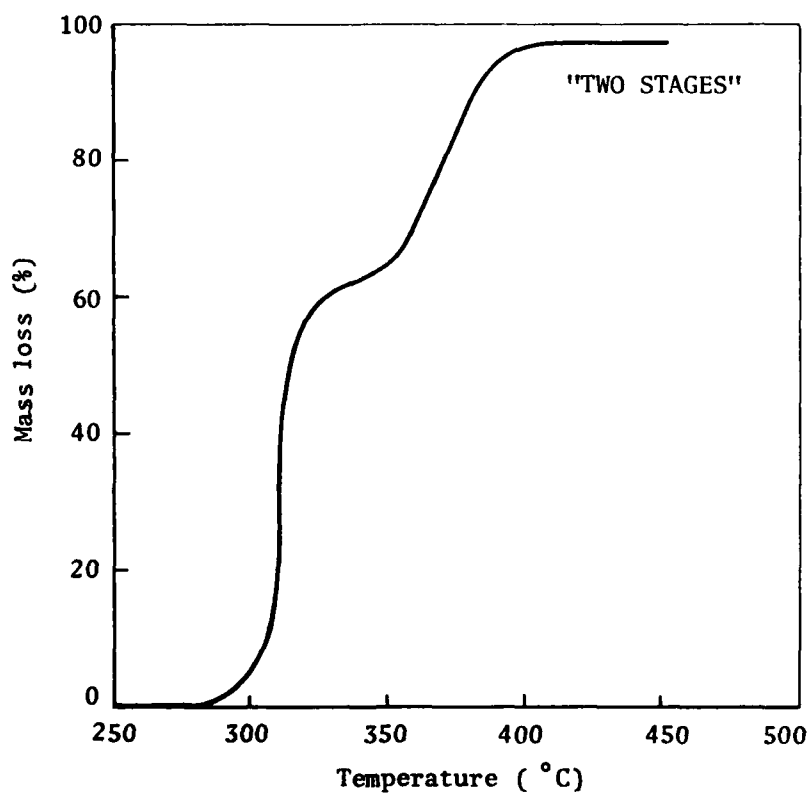
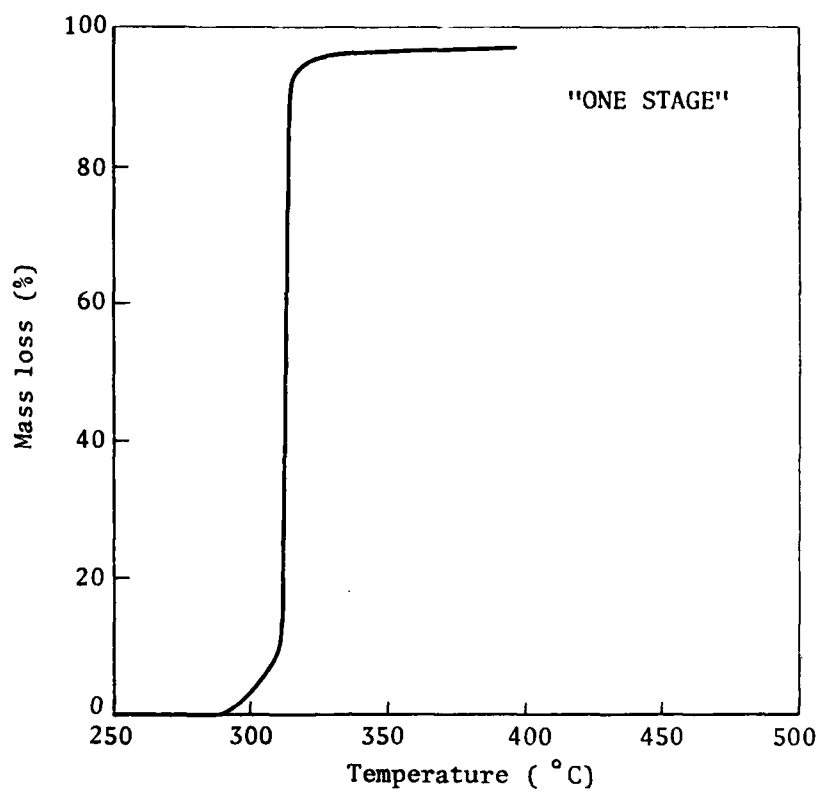


Figure 3. Thermogravimetric Analysis

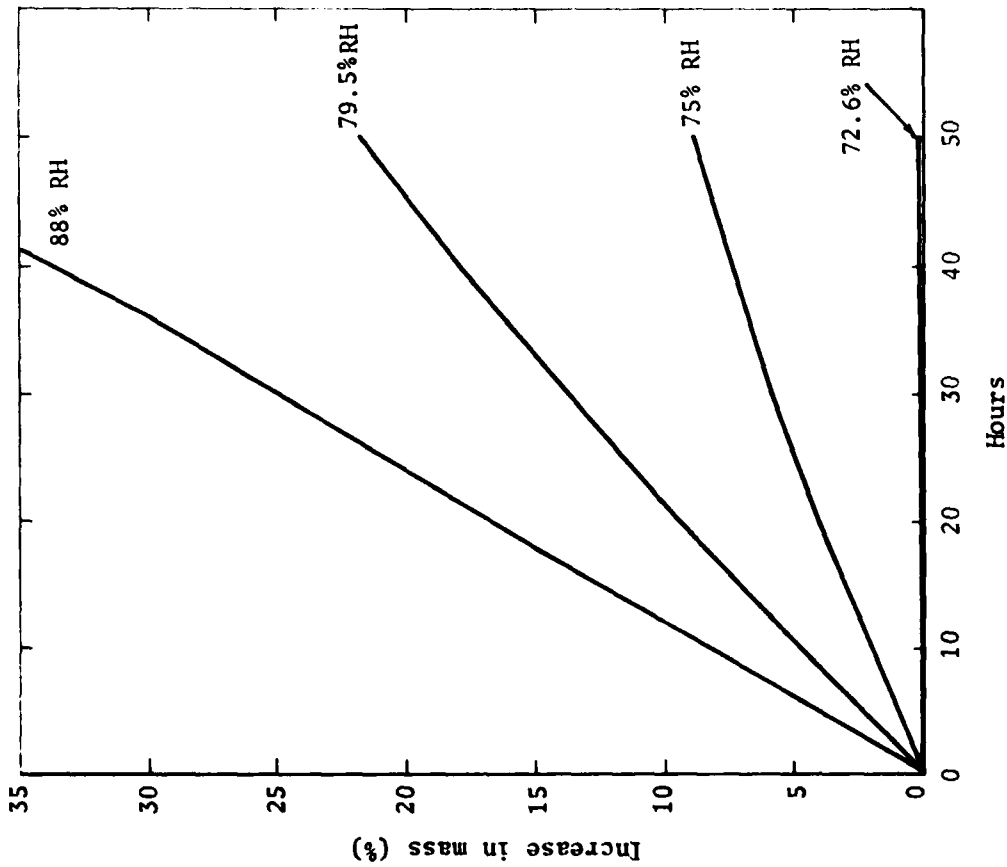
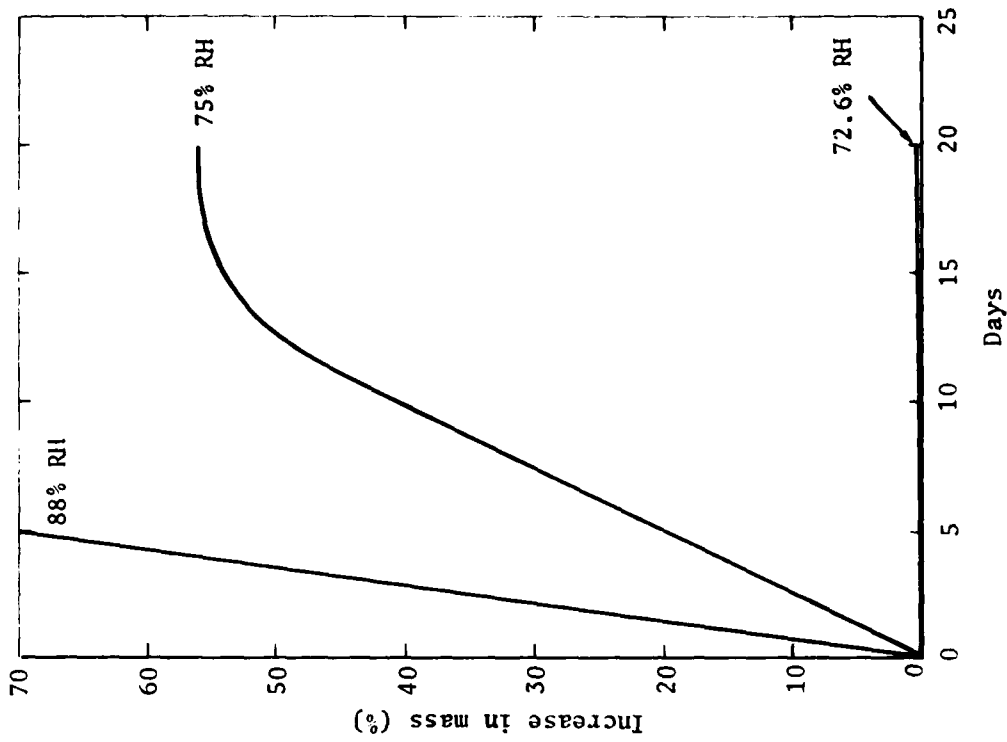


Figure 4. Hygroscopicity of MAP at 20°C

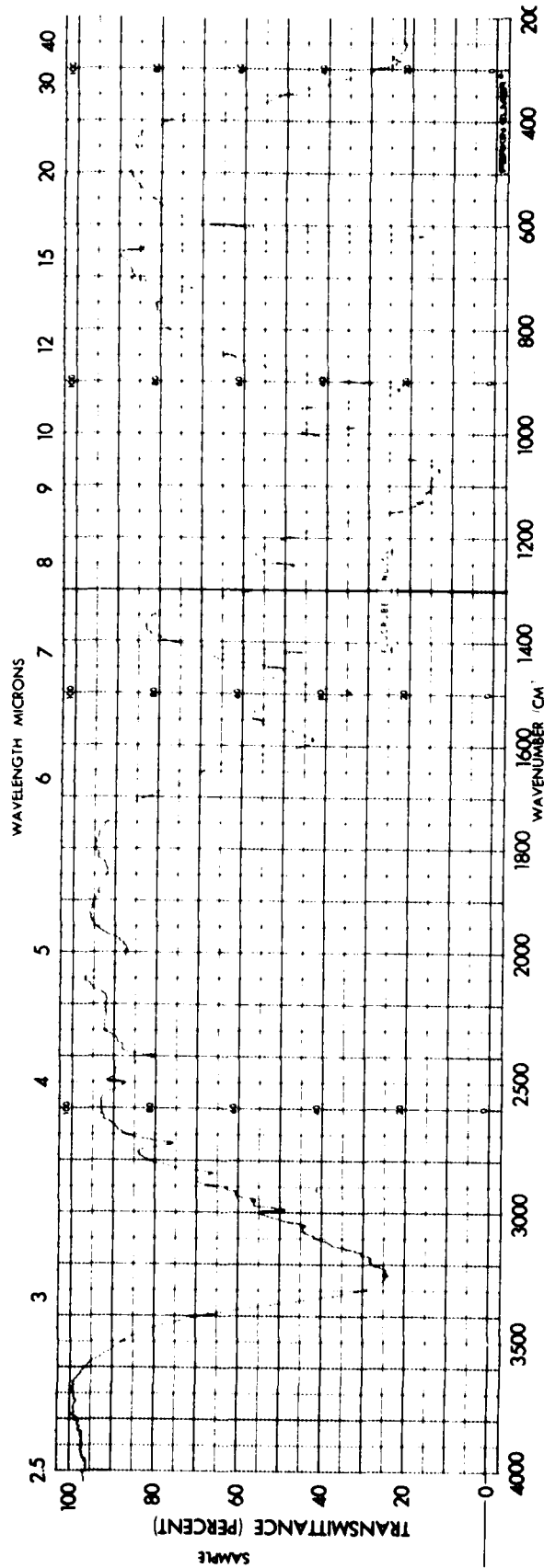


Figure 5. Infrared spectrum of MAP

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| In United States of America | |
| Counsellor, Defence Science, Washington | 2 |
| In Australia | |
| Chief Defence Scientist | 3 |
| Executive Controller, Australian Defence Scientific Service | 4 |
| Superintendent, Defence Science Administration Division | 5 |
| Director, Joint Intelligence Organisation (DDSTI) | 6 |
| Defence Information Services Branch (for microfilming) | 7 |
| Defence Information Services Branch for: | |
| United Kingdom, Ministry of Defence, Defence Research Information Centre (DRIC) | 8 |
| United States, Department of Defense, Defense Documentation Center | 9 - 20 |
| Canada, Department of National Defence, Defence Science Information Service | 21 |
| New Zealand, Ministry of Defence | 22 |
| Australian National Library | 23 |
| Superintendent, Physical Chemistry Division, Materials Research Laboratories | 24 |
| Head, Explosives and Ammunition Composite, Materials Research Laboratories | 25 |
| Deputy Controller, Munitions Supply Division | 26 |
| Manager, Explosives Factory, Maribyrnong | 27 |
| Defence Library, Campbell Park | 28 |
| Library, Aeronautical Research Laboratories | 29 |
| Library, Materials Research Laboratories | 30 |
| WITHIN DRCS | |
| Chief Superintendent, Weapons Systems Research Laboratory | 31 |
| Superintendent, Propulsion and Marine Physics Division | 32 |
| Senior Principal Research Scientist, Propulsion Composite | 33 |
| Principal Officer, Propellants and Polymers Group | 34 |
| Mr J. Hooper, Propellants and Polymers Group | 35 |
| Principal Officer, Combustion and Explosives Group | 36 |
| Mr I.R. Johnston, Combustion and Explosives Group | 37 |

Mr P.E. Rogasch, Combustion and Explosives Group

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Mr R.H. Weldon, Combustion and Explosives Group

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