

**NATO STANDARD**

**AOP-4682**

**ENERGETIC MATERIALS  
TEST METHODS  
FOR INGREDIENTS**

**Edition A Version 1  
MAY 2018**



**NORTH ATLANTIC TREATY ORGANIZATION**

**ALLIED ORDNANCE PUBLICATION**

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**NATO STANDARDIZATION OFFICE (NSO)**

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<b>CHAPTER 1 INTRODUCTION</b>
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**1.1 SCOPE**

1. The aim of this AOP is to standardize test procedures for quality specifications of ingredients in military energetic materials. It deals with chemical and physical laboratory test methods, except those, which are covered by method-standards and AOP-48.

2. The test procedures and specifications were developed to facilitate cross procurement and certification of the ingredients and provide a means by which countries can be satisfied with the quality of these ingredients by making them suitable for military use within NATO.

3. Test procedures described in this AOP replace those previously described in the following STANAGs for ingredients: 4021, 4022, 4023, 4024, 4025, 4026, 4230, 4284, 4299, 4300, 4543, 4566, 4583, 4679, 4700 and 4719.

4. STANAG 4178 covers the chemical and physical testing of nitrocellulose because most of its test methods are unique to that material. Therefore this AOP does not deal with chemical and physical tests for nitrocellulose.

5. This AOP will be reviewed upon the request of a participating nation. If any changes are proposed, the national delegate of the submitting country shall request that the Chairperson of AC/326 subgroup A includes this as an agenda item for the next meeting of the subgroup.

6. Requests to revise this AOP must be accompanied by supporting documentation and should be presented to the Chairman of AC/326 subgroup A for inclusion in the agenda of the next meeting of the subgroup. Subgroup A will rewrite and approve the revisions of this AOP. Such revisions will be provided to the Custodian Nation and to the international staff secretary for publication. Austria is the Custodian Nation for this document.

7. The criteria to be met by any given ingredient for tests performed under this AOP will be given in the specific STANAG for that ingredient. Changes in the acceptable values of properties for an ingredient must be subject to ratification by the participating nations and are therefore included in the ingredient STANAGs and not in this test manual.

8. Warning: This AOP calls for the use of substances and test procedures that may be injurious to health if adequate precautions are not taken. It refers only to technical suitability and in no way absolves the user from the statutory obligations relating to health and safety at any stage during use.

## 1.2 RELATED DOCUMENTS

- STANAG 4021 Ed. 3, Specification for CE (Tetryl) for deliveries from one NATO nation to another
- STANAG 4022 Ed. 4, Specification for RDX (Hexogene)
- STANAG 4023 Ed. 5, Specification for PETN (Penthrite or Nitropenta) from one NATO nation to another
- STANAG 4024 Ed. 3, Explosives - Specification for Ammonium nitrate (for use in explosives)
- STANAG 4025 Ed. 3, Specification for TNT (Tolite, Trinitrotoluene) for deliveries from one NATO nation to another
- STANAG 4026 Ed. 3, Explosives - Specification for Picrite (Nitroguanidine, NQ)
- STANAG 4178 Ed.2, Test procedures for assessing the quality of delivery of Nitrocellulose from one NATO nation to another
- STANAG 4230 Ed. 1, Explosives - Specification for HNS (Hexanitrostilbene) for deliveries from one NATO nation to another
- STANAG 4284 Ed. 1, HMX (Octogene), physical and chemical requirements, specification for deliveries from one NATO nation to another
- STANAG 4299 Ed. 1, Specification for AP (Ammonium perchlorate) for deliveries from one NATO nation to another
- STANAG 4300 Ed. 1, Test procedures for assessing the quality of Aluminium Powder for use in explosive formulation, for deliveries from one NATO nation to another
- STANAG 4543 Ed. 1, Explosives - Specification for NTO (3-Nitro-1,2,4-triazol-5-one) for deliveries from one NATO nation to another
- STANAG 4566 Ed. 1, Explosives - Specification for CL20 (Hexanitrohexaazaisowurtzitane) for deliveries from one NATO nation to another
- STANAG 4583 Ed. 1, Chemical test procedures for n-Butyl-2-Nitratoethyl-Nitramine (n-Butyl NENA)
- AOP 4679 Ed. 1, Red Phosphorus, Amorphous, Microencapsulated (for use in pyrotechnics)
- STANAG 4700 Ed. 1, Energetic materials - Specification for GUDN (Guanylureadinitramide)
- STANAG 4719, Ed 1, Energetic materials - Specification for TEGDN (Triethyleneglycoldinitrate)

### 1.3 Summary of applied methods for different ingredients

#### 1.3.1 Physical Properties

Table 1.3.1- Physical properties: collection of tests (x= addressed in ingredient STANAG)

Property	4021 CE	4022 RDX	4023 PETN	4024 AN	4025 TNT	4026 NQ	4230 HNS	4284 HMX	4299 AP	4300 AI	4543 NTO	4566 CL20	4583 BuNENA	4679 RP	4700 GUDN	4719 TEGDN
<b>2 Solid state properties</b>																
2.1 Melting point	X	X	X		X		X	X								
2.1.1 Capillary tube method	X	X	X				X	X								
2.1.2 Solidification point					X											
2.2 Particle density												X				
2.2.1 Gas pycnometer												X				
2.2.2 Flotation density												X				
2.2.3 Liquid pycnometer												X				
2.3 Bulk density										X						
2.4 Granulation		X	X	X			X			X	X	X		X		
2.4.1 Dry sieving																
2.4.2 Wet sieving																
2.4.3 LALLS																
2.5 Specific surface																
2.5.1 BET-Analysis						X	X									

### 1.3.2 Chemical Properties – General Wet Chemistry

Table 1.3.2- Chemical properties, general wet chemistry: collection of tests (x= addressed in ingredient STANAG)

Property	4021 CE	4022 RDX	4023 PETN	4024 AN	4025 TNT	4026 NQ	4230 HNS	4284 HMX	4299 AP	4300 AI	4543 NTO	4566 CL20	4583 BuNENA	4679 RP	4700 GUDN	4719 TEGDN
<b>3 General wet chemistry</b>																
3.1 Acidity and Alkalinity	X	X	X	X	X	X	X	X			X	X	X		X	X
3.1.1 Standard acid/base titration	X	X	X	X	X	X	X	X					X			
3.1.2 Titration with TBAH in solvent-system											X	X				
3.1.3 determination of pH-value in defined solution															X	
3.2 Moisture content				X	X				X				X		X	
3.2.1 KF, coulometric				X	X				X				X		X	
3.2.2 KF, volumetric				X	X				X				X		X	
3.3 Total volatiles	X			X		X	X			X	X			X	X	
3.3.1 Heating and reweighing	X			X		X	X			X	X				X	
3.3.2 Vacuum and reweighing														X		
3.4 Insoluble impurities	X	X	X	X	X	X	X	X	X	X		X		X		
3.4.1 Dissolving and reweighing	X	X	X	X	X	X	X	X	X	X		X				
3.4.2 Insoluble in aqua regia														X		
3.5 Soluble impurities				X			X		X	X						
3.5.1 Soxhlet extraction				X					X	X						
3.5.2 Water soluble impurities							X									



Table 1.3.2 (continued)- Chemical properties, general wet chemistry: collection of tests (x= addressed in ingredient STANAG)

3.6 Inorganic matter (ash)	X	X		X	X	X	X	X	X							
3.6.1 Incineration in oven	X	X						X								
3.6.2 Sulfated ash					X	X	X		X							
3.7 Gritty particles	X	X	X	X	X	X	X	X	X	X					X	
3.7.1 Direct extraction on sieve																
3.7.2 Dissolving and filtering over crucible																

### 1.3.3 Chemical Properties – Specific Wet Chemistry

Table 1.3.3- Chemical properties, specific wet chemistry: collection of tests (x= addressed in ingredient STANAG)

Property	4021 CE	4022 RDX	4023 PETN	4024 AN	4025 TNT	4026 NQ	4230 HNS	4284 HMX	4299 AP	4300 AI	4543 NTO	4566 CL20	4583 BuNENA	4679 RP	4700 GUDN	4719 TEGDN
<b>4 Specific wet chemistry</b>																
4.1 Determination of Ammonium				X					X							
4.2 Determination of Chloride				X					X							
4.3 Determination of Sulfate				X					X							
4.4 Determination of Nitrite				X												
4.5 Determination of Nitrate									X							
4.6 Determination of active aluminium										X						

## 1.4 REQUIREMENTS FOR LABORATORY EQUIPMENT

### Analytical balance:

Procedures are dimensioned to provide sufficient precision on use of an analytical balance with the capability to ensure an accuracy of 0.1 mg.

### Thermometer:

Thermometers for determination of the melting point have to ensure accuracy of 0.1°C.

Thermometer for TNT-solidification needs an accuracy of 0.01°C in the interval from 79 to 81°C.

Thermometers should be calibrated every 5 years.

### Analytical volumetric glassware (burettes, pipettes, flasks, ....):

Calibration should take place every 1 to 3 years

### Accuracy of volumetric pipettes:

Volume	Accuracy
1 ml	± 0.007 ml
2.5 ml	± 0.01 ml
5 ml	± 0.015 ml
10 ml	± 0.02 ml
20 ml	± 0.03 ml
25 ml	± 0.03 ml
40 ml	± 0.05 ml
50 ml	± 0.05 ml
100 ml	± 0.120 ml

### Accuracy of micro burettes:

Total volume: 2 ml with an accuracy of 0.01 ml.

Analytical volumetric plastic-ware:

Calibration should take place every 3-12 months

Piston-operated pipettes with replaceable tips:

Volume of transfer up to 10  $\mu\text{L}$ : accuracy 1%

Volume of transfer up to 50  $\mu\text{L}$ : accuracy 0.5%

Volume of transfer above 50  $\mu\text{L}$ : accuracy 0.2%

Additional laboratory equipment:

Apparatus for determination of active aluminium

Apparatus for determination of solidification point

Automated potentiometric titrator

Density/specific gravity meter

Desiccator

Drying cabinet

Drying oven

Fritted crucibles, porosity D3, D4

Gas pycnometer

Karl-Fischer Titrator

LALLS(Low angle laser light scattering)-spectrometer

Liquid pycnometers

Magnetic stirrer

Mechanical tapping device for determination of tap density

Melting point apparatus for capillary tubes, heating-rate  $1^\circ/\text{min}$

Micro-syringes

Muffel furnace (min.  $700^\circ\text{C}$ )

Nitrogen adsorption instrument

Petri dishes

pH-meter

Water-bath

Semi-micro burette

Set of standard sieves and sieving apparatus

Soxhlet extractors

Spectrophotometer (VIS)

Teflon separatory funnels (125 ml)

Vacuum oven

Volumeter

Wash bottle

## 1.5 CHEMICALS

Chemicals and the degree of purity to be provided are listed below. The chemicals have to be analytical grade ("pro analysis").

Acetic acid, glacial

Acetone

Acetonitrile

Aerosol OT

Ammonium perchlorate (nitrate free)

Ammonium thiocyanate, solution; 0,1 N

Barium chloride

Benzoic acid

Bromocresol green indicator

Bromothymol blue indicator

Calcium chloride, desiccant

Carbon black

Chromosulfuric acid

Dibromomethane

Diethyl ether

DMF (Dimethylformamide)

DMSO (Dimethylsulfoxide)

Diethyl-sodium sulfosuccinate

Disodium tartrate dihydrate

Formaldehyde solution, 37%, stabilized with 10% methanol

Helium, gas

HCl, concentrated

Iron(III)ammonium sulfate

Isopropanol

Karl-Fischer-reagent

Lithium chloride

Methanol

Meta-phenylene diamine; 0.5% aqueous solution

Methylred/Methylene blue indicator

1-Naphthylamine-7-sulfonic acid  
Nitric acid, concentrated  
Nitric acid, solution; 2 M  
Nitrobenzene  
Nitrogen, gas  
Nitrogen, liquid  
Oxalic acid dihydrate  
Phenolphthalein  
Potassium hydrogen phthalate  
Pyridine  
Silver nitrate, solution; 0.02 N  
Silver nitrate, solution; 0.1 N  
Sodium carbonate  
Sodium hydrogen carbonate  
Sodium hydroxide; 20% solution  
Sodium hydroxide; 0.1 N solution  
Sodium hydroxide; 0.02 N solution  
Sodium nitrite  
Sulfanilic acid  
Sulfuric acid; 0.01 N solution  
Sulfuric acid; concentrated  
TBAH (Tetra-butylammonium hydroxide) in Isopropanol; 0.1 N  
TBAH in THF; 0.05 N  
THF (Tetrahydrofuran)  
Toluene  
Tricalcium phosphate  
Zinc dust

## 1.6 SCOPE OF PRECISION STATEMENTS IN AOP-4682 (A)(1)

### 1.6.1 Principles of Uncertainty of Measurements

Uncertainty is a parameter associated with the result of a measurement that characterises the dispersion of the values that could reasonably be attributed to the measurand. If the uncertainty is expressed as a standard deviation, this is called a standard uncertainty. It is a quantification of the doubt about the measurement result and is based on principles of statistics.

In other words, uncertainty is the quantification of the qualitative concept of accuracy of measurements as it is defined in ISO 5725. Accuracy is governed by two types of contribution, trueness and precision.

Trueness refers to the closeness of agreement between the average value obtained from a large series of test results and an accepted reference value and represents the systematic error of a measurement.

Precision is the closeness of agreement between independent test results obtained under stipulated conditions. Precision measures include *repeatability* (variability observed in a laboratory over a short time with same operator, equipment and sample) and *reproducibility* (variability when different laboratories analyse the same sample). Precision covers the randomly introduced error of a measurement.

In practice, for most cases precision will be *the essential component of overall uncertainty*.

*It has to be emphasized, that precision statements given in this AOP refer to this randomly introduced part of uncertainty by the measurement procedure!*

The uncertainty of the total result is subject to several additional parameters which even might give a larger contribution than precision of the measurement procedure.

*The main factor of uncertainty in many cases will be improper sampling with respect to inhomogeneity of the sample.*

*The description of the methods of this AOP starts at the level of a single sample and precision statements are only covering this step of chemical analysis.*

*The choice of a proper sampling strategy is not within the scope of this manual!*

### 1.6.2 Calculation of Precision

Precision summarizes all factors which are randomly affecting the result. Due to its anticipated random-nature it is calculated as a standard deviation.

It has to be kept in mind that precision can vary considerably with concentration levels.

For practical purpose it is feasible to calculate the precision separately for different steps of a procedure, as this enables to identify critical steps and modify such steps for better performance of the overall-procedure. Combined precision is calculated by use of law of propagation.

The standard deviation is calculated according to statistic definitions. If a measurand is calculated from several steps of operation, a combined uncertainty can be calculated according to the law of propagation of errors.

In analytical chemistry usually the so called expanded uncertainty is used. This value provides an interval within which the value of the measurand is believed to lie with a higher level of confidence.

The expanded uncertainty is calculated by multiplying the standard deviation by a certain factor  $k$  (for  $k=2$ ; the confidence interval is 95%, for  $k=3$ , it is 99.7%).

Spreadsheet methods have been developed for simplified calculation. For further details it is referred to "EURACHEM/CITEC Guide Quantifying Uncertainty in Analytical Measurement" (ISBN 0948926155).



## 1.7 ABBREVIATIONS

AN	Ammonium nitrate
AP	Ammonium perchlorate
BET	Brunauer-Emmett-Teller-Analysis
BuNENA	Butylnitratoethylnitramine
CE	Tetryl
CL-20	Hexanitrohexaazaisowurtzitane
DMF	Dimethylformamide
DMSO	Dimethylsulfoxide
DNT	Dinitrotoluene
GUDN	Guanylureadinitramide
HMX	Octogene
HNS	Hexanitrostilbene
ID	Inner diameter
ISO	International Organization for Standardization
KF	Karl-Fischer-Titration
LALLS	Low angle laser light scattering
NC	Nitrocellulose
NQ	Nitroguanidine
NTO	3-Nitro-1,2,4-triazol-5-one
OD	Outer diameter
PETN	Pentaerythritol tetranitrate (Penthrite)
RDX	Hexogene
RP	Red phosphorous
TBAH	Tetra-butylammonium hydroxide
TEGDN	Triethyleneglycoldinitrate
THF	Tetrahydrofurane
TNT	Trinitrotoluene
VIS	Visible Light

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<b>CHAPTER 2    SOLID STATE PROPERTIES</b>
--

**2.1    MELTING POINT OR SOLIDIFICATION POINT****2.1.1    Capillary Tube Method**Principle

The method consists of determining the melting point of the sample crystals introduced into a capillary tube and heated at the defined rate.

Applicability

The method can be used for melting point determination of CE, RDX, PETN, HNS and HMX. The specifics applied for these ingredients in this method are summarized in the following table:

Table 2.1.1.1 - Start temperature ( $T_{\text{start}}$ ), end temperature ( $T_{\text{end}}$ ) and minimum temperature divisions ( $\Delta T$ ) of the thermometer used

<b>Ingredient</b>	<b><math>T_{\text{start}}</math> (°C)</b>	<b><math>T_{\text{end}}</math> (°C)</b>	<b><math>\Delta T</math> (°C)</b>
CE	120	135	0.1
RDX Type A	190	205	0.1
RDX Type B	180	195	0.1
PETN	130	145	0.1
HNS	280	330	0.5
HMX	260	300	0.5

Equipment

Any melting point apparatus, which can be controlled to heat the sample at a rate of 1°C per minute in the specified temperature range  $T_{\text{start}}$  to  $T_{\text{end}}$ .

A suitably calibrated thermometer covering not less than the range  $T_{\text{start}}$  to  $T_{\text{end}}$  and graduated in  $\Delta T$  divisions. Calibrated thermocouples can be used instead.

Melting point tubes, thin-walled and closed at one end. Size of the tubes depends on type of melting point apparatus used (typically 1.8 mm OD x 1.6 mm ID x 90 mm length).

Procedure

Introduce enough of the dried pulverized sample into a melting point tube to fill the tube to a depth of 10 millimetres. A different amount of sample can be used if required by the operating instructions for the melting point apparatus. Adjust the control of the melting point apparatus to bring the temperature quickly to temperature  $T_{\text{start}}$ .

Reduce the rate of heating to 1°C per minute and insert the melting point tube into the apparatus. Position the sample not more than 3 mm adjacent to and vertically even with the mercuric bulb of the thermometer or thermocouple.

Note the temperature when the material starts to melt as  $T_1$ . The material may slump and change color as the melting point is approached. This appearance should not be confused with the appearance of liquid.

Follow the process and note  $T_2$  as the temperature when all the material has just fully melted.

Alternatively, the melting point can be detected using a thermocouple positioned in the sample material so that it reaches the bottom of the melting point tube. The melting process is marked in the recorded temperature-time curve by a momentary pause in the rate of temperature increase (point of coalescence). Onset point of this process corresponds to melting point of the sample.

### Expression of the results

Apply any correction necessary to the calibrated thermometer or thermocouple. Report the observed temperature to the nearest 0.1°C as the melting point.

Calculate as follows:

$$\text{Melting Point [}^\circ\text{C]} = [(T_1 + C_1) + (T_2 + C_2)]/2 + C_3 \quad (\text{eq. 2.1.1.1})$$

$C_1, C_2$ : corrections of bore errors at readings  $T_1$  and  $T_2$  (all in [°C])

$$C_3 = 0.00016 * N * (T - t); \quad (\text{eq. 2.1.1.2})$$

$T$  = indicated temperature

$t$  = average ambient temperature, indicated by a second thermometer, whose bulb is near the mid-point of the exposed mercury column (all in [°C]).

$N$  = the number of degree divisions in the length of the exposed column of Mercury

### Precision

Reproducibility of the result has to be shown to be within  $\pm 0.2^\circ\text{C}$  (95% probability) for melting points below 200°C and within  $\pm 1^\circ\text{C}$  (95% probability) above 200°C, which refers to a standard deviation of  $\pm 0.1^\circ\text{C}$ , and  $\pm 0.5^\circ\text{C}$  respectively.

### 2.1.2 Solidification Point

#### Apparatus

Suitable apparatus for the determination of the crystallizing point is shown in annex A, Fig.1. If the outer bottle is not of amber glass, an aluminium screen should be placed round the apparatus to protect the sample from direct sunlight during the test.

The standard thermometer must be accurately calibrated (to 0.01°C) over the range 79 to 81°C at least.

#### Applicability

This method is used for TNT.

#### Procedure

Melt about 50 g of sample in a covered beaker by immersing the beaker in a water bath at 95 to 100°C or placing it in a suitable oven. Pour the melt into the inner tube of the apparatus to a level between 25 and 35 mm from the top. At this stage, the melt should be at a temperature of not less than 85°C; if necessary, reheat the tube in a hot water bath and then return it to the apparatus. Insert the thermometer and stirrer, preferably pre-heated to avoid encrustation with solid TNT, so that the bulb is located centrally in the tube and about 25 mm from the bottom, and stir the melt continuously by vertical movement of the stirrer. Observe the temperature, which will fall steadily and then begin to rise as crystallization sets in. Discontinue stirring at this stage and note the minimum temperature reached.

The temperature will rise to a maximum and remain steady for some minutes. Tap the thermometer gently to ensure that the mercury is not sticking and record this maximum temperature.

**NOTE:** If the amount of super-cooling exceeds 1.5°C, the observed setting point may be lower than the true figure and the operation should then be repeated on a fresh sample. In this context, "super-cooling" refers to the difference in temperature between the maximum temperature recorded during solidification of the melt and the minimum temperature recorded before solidification begins.

#### Calculation

Report the maximum temperature recorded as described under "Procedure" as the crystallizing point unless a total immersion thermometer has been used and there is a significant length of mercury thread exposed above the sample. In this case, it is necessary to apply a correction for emergent stem. The correction is added to the observed temperature and is calculated from the formula:

$$C = 0.00016 \cdot (T_0 - T_1) \cdot N \quad (\text{eq. 2.1.2.1})$$

where:

C = correction in °C

0.00016 = apparent expansion of mercury in glass

T<sub>1</sub> = the observed reading in °C

T<sub>0</sub> = the mean temperature of the exposed column of mercury as indicated by the thermometer adjacent to the middle of the emergent stem

N = the number of degree divisions in the length of the exposed column of Mercury

### Precision

Reproducibility of the result has to be shown to be within  $\pm 0.1^\circ\text{C}$  (95% probability), which refers to a standard deviation of  $\pm 0.05^\circ\text{C}$ .

## **2.2 PARTICLE DENSITY**

### **2.2.1 Gas Pycnometer Density**

#### Principle

The density of the substance is determined by using a commercial gas pycnometer, which analyses the remaining gas-volume in the measurement by comparison with that of a reference cell.

#### Test apparatus

Commercial gas pycnometer

Solid objects of known volume are also needed for the calibration of the pycnometer

Procedure

Weigh accurately a 25 g sample of the substance (or the amount appropriate for the pycnometer being used) to the nearest 0.01 g ( $w_1$ ). Determine the volume of the weighed specimen as directed by the operating instructions supplied with the pycnometer ( $V$ ). Calculate the density of the sample with the following equation:

$$\text{Density} = \frac{w_1}{V} \text{ [g/ml]} \quad (\text{eq 2.2.1.1})$$

where  $V$  is in ml

Precision

Example:  $w_1$ : 25.00 g     $\Delta w_1$ : 0.01 g     $V$ : 12.5 ml     $\Delta V$ : 0.1 ml

Density = 2.000 g/ml

Standard uncertainty: 0.016 g/ml (0.79% rel)

Simplified approach: the uncertainty is estimated by 100% ( $\Delta w_1/w_1 + \Delta V/V$ ) = 0.84% rel

**2.2.2 Flotation Density**Principle

The density of the substance is determined by matching its density with a mixture of toluene and dibromomethane across the range needed to separate all the substance in a sample. This method has the advantage of giving a distribution rather than a single value but is labour intensive.

Test Apparatus

- density/specific gravity meter
- several 125 ml Teflon separatory funnels (normally 8)
- matching number of 30 ml medium fritted crucibles

Procedure

Prepare a stock solution with a theoretical density just above the expected density of the substance (approximately 0.005 g/ml above) by mixing the proper amounts of toluene (0.866 g/ml) and dibromomethane (2.477 g/ml) in a beaker. Verify that 100% of your substance are floating. Remove a 40 ml aliquot of the prepared flotation mixture and add it to the separatory funnel. Weigh accurately a 5 g sample ( $w_1$ ) of the substance sample into the funnel. Shake well to wet the substance. Allow the mixture

to separate and settle for approximately 2 hours. Prepare a second 40 ml sample with a density reduced by approximately 0.005 g/ml by adding 0.2 to 0.5 ml of toluene to the original sample. Verify the density with the specific gravity meter. Prepare another 5 g substance sample and shake in a separatory funnel and allow to settle. Continue until all the substance is more dense than the solution. Allow all the substance samples to fully reach equilibrium. Filter the substance that has settled out through the clean tared medium fritted crucible ( $w_2$ ). Place the crucible in a 100°C oven for 2 hours. Cool in a desiccator to room temperature. Reweigh the crucible ( $w_3$ ). **(Note: The substance should be removed from the fritted crucible using a solvent to dissolve it. It should not be scraped off the frit due to the sensitivity).** From this, calculate the amount of the substance recovered (with density higher than the solvent density) for each solvent density according to the following equation:

$$\% \text{ recovered} = \frac{(w_3 - w_2) * 100}{w_1} \quad (\text{eq. 2.2.2.1})$$

The average density of the sample is reported as the density of the solvent at which 50% of the substance is recovered. Since the 50% value will normally not fall exactly on a solvent density point selected, the 50% number will be determined by a linear interpolation from the nearest two points.

### Precision

The solutions for flotation separation are prepared at a step-wise change of 0.005 g/ml. Precision of the density is determined by precision of the used gravity meter. It can be anticipated with 0.25%rel.

## 2.2.3 Liquid Pycnometry

### Principle

The density of a solid is measured by filling a tared, calibrated volumetric container (pycnometer) with the solid and back filling with distilled water containing surfactant. Results are reported as g/ml at the conditioned temperature.

### Test Apparatus

- specific gravity bottle, pycnometer
- constant temperature bath controlled to 0.1°C
- analytical balance accurate to 0.1 mg
- desiccator



Reagents

- distilled water containing 1% aerosol OT or other suitable surfactant

Step No1: Pycnometer Calibration

Weigh the clean dry pycnometer on the analytical balance ( $w_1$ ). Fill the pycnometer with freshly distilled water at room temperature. Replace the top on the pycnometer. Place the pycnometer in the constant temperature bath at near 25°C for at least 30 minutes to reach equilibrium temperature. During conditioning, the pycnometer top should always have a small bead of distilled water covering the capillary to prevent loss of water by evaporation through the capillary. Remove the pycnometer from the bath, push the top down tight and immediately wipe the top with a non-absorbent material so that the liquid level in the pycnometer is absolutely flush with the top of the lid. Wet the outside of the pycnometer, except the lid, with acetone and evaporate the acetone by blowing oil-free air or nitrogen on the pycnometer. Repeat until dry and cool. Wipe finally with a dry, clean, lint-free cloth being careful not to warm with the hands. Weigh the filled pycnometer on an analytical balance ( $w_2$ ). Determine the exact volume ( $V$ ) of the pycnometer with the following calculation:

$$\text{Volume of pycnometer}(V) = \frac{(w_2 - w_1)}{d_1} \quad (\text{eq. 2.2.3.1})$$

$d_1$  is the density of distilled water at the bath temperature

Step No.2: Determination of Density of Surfactant Solution

The density of the surfactant solution at the bath temperature can be determined by filling the clean dry pycnometer with the solution and conditioning it at the test temperature as described above. After conditioning, the weight ( $w_3$ ) of the filled pycnometer is determined accurately. The density of the solution is calculated using the following equation:

$$d_2 = \frac{(w_3 - w_1)}{V} \quad (\text{eq.2.2.3.2})$$

where  $d_2$  is the density of the surfactant solution [g/ml] at the bath temperature

$V$  is the volume of the pycnometer (ml)

Step No.3: Determination of Solid Sample Density

Weigh to the nearest 0.2 mg a sufficient amount of the substance into the pycnometer to fill it about one third full ( $w_4$ ). Fill the pycnometer the rest of the way with the surfactant solution. Place the pycnometer under light vacuum to remove any bubbles adhering to the surface of the substance particles. Lightly place the top on the pycnometer and immerse it in a bath of distilled water in a small beaker. Place

the beaker with the pycnometer in the temperature-controlled bath and allow it to equilibrate at least 30 minutes. Dry the pycnometer as in the calibration procedure. Weigh the filled and externally dry pycnometer ( $w_5$ ). Determine the material density using the following equation:

$$\text{Density of material} = \frac{w_4 * d_2}{w_4 + w_3 - w_5} \text{ [g/ml]} \quad (\text{eq.2.2.3.3})$$

Precision:

**Example:**

A pycnometer with a volume of 25 ml typically would give the following result:

$w_1=11.500 \text{ g}$	$\Delta w_1=0.0002 \text{ g}$
$w_2=36.500 \text{ g}$	$\Delta w_2=0.0002 \text{ g}$
$d_1=0.9982 \text{ g/ml}$	$\Delta d_1=0.0001 \text{ g/ml}$
Standard uncertainty of volume: 0.01%rel	

A typical measurement could result in:

$w_3= 36.500 \text{ g}$	$\Delta w_3=0.0002 \text{ g}$
$w_4=16.000 \text{ g}$	$\Delta w_4=0.0002 \text{ g}$
$w_5= 44.500 \text{ g}$	$\Delta w_5=0.0002 \text{ g}$
$d_2=0.9982 \text{ g/ml}$	$\Delta d_2=0.0001 \text{ g/ml}$

Standard uncertainty of density: 0.020%rel.

Simplified approach:  $100\% * (\Delta w_4 / (w_3 + w_4 - w_5) + \Delta d_2 / d_2) = 0,023\%$

## 2.3 BULK DENSITY

The term bulk density includes the properties apparent density and tap density. These properties differ in the effect of compressibility of a powder sample.

The apparent density is the weight of a unit volume of loose powder. It strongly depends on the particle size and usually decreases with decreasing particle size.

It also decreases as the particle shape becomes more irregular and with increasing surface roughness. It also depends on particle size distribution. In the case of a wide range of particle size the apparent density increases because the space between coarse particles is filled with smaller particles.

### 2.3.1 Apparent Density

Apparent density can be determined using one of three methods.

#### Cylinder Method

A sufficient quantity of powder is passed through a sieve with apertures greater than or equal to 1.0 mm to break up agglomerates that may have formed during storage. The material then is gently poured into a dry graduated cylinder of 250 ml (readable to 2 ml) without compacting. The sample weight should be approximately 100 g, weighed with 0.1% precision.

The powder is levelled carefully without compacting and the unsettled apparent volume is read to the nearest graduated unit. The quantity of the powder should be chosen to achieve a volume between 150 and 250 ml.

#### Funnel-Method

This method uses standardized funnels eg. the Hall funnel or the Carney funnel, which differ in diameter of the orifice of the funnel. The powder is poured through the funnel under standardized conditions into a 25 ml cylinder or cup until it is slightly overfilled. The excess powder is levelled off using a spatula and the filled cylinder or cup is weighed.

#### Volumeter-Method

A volumeter is an apparatus which consists of a top funnel with a 1.0 mm sieve. The funnel is mounted over a baffle box containing four glass baffle plates over which the powder slides and bounces as it passes. At the bottom of the baffle box a funnel collects the powder and allows it to pour into a cup of defined volume (usually 25 ml). The cup is slightly overfilled and excess powder is removed by levelling carefully with the edge of the blade of a spatula. The mass of the filled cup is determined to the nearest 0.1%.

#### Precision:

Precision of the balance should allow a determination of the weight at least for 0.05 g.

It should be possible to determine apparent density with a precision of 0.1%.

### 2.3.2 Tap Density

The tap density is an increased bulk density attained after mechanically tapping the powder sample in a certain container.

The tapped density is obtained by mechanically tapping a graduated measuring cylinder or vessel containing the powder sample. After observing the initial powder volume, the measuring cylinder or vessel is mechanically tapped until little further volume change is observed.

The mechanical tapping is achieved by raising the cylinder or vessel and allowing it to drop a specified distance under its own mass. Drop-height usually is specified with 3 mm, tapping frequency between 100 and 300 taps/min.

Precision:

Precision of the balance should allow a determination of the weight at least for 0.05 g.

Results will be strongly depending on procedure and apparatus. Results should be obtained with an uncertainty better than 0.1 g/ml.

## 2.4 GRANULATION

Four general procedures are possible:

- dry sieving
- wet sieving
- photometric analysis and
- LALLS (low-angle laser light scattering)

Dry sieving is used for characterization of ammonium nitrate only. To prevent caking, an anti-caking agent, such as carbon black, tricalcium phosphate can be added at an amount of approximately 1%.

If a substance has a tendency for agglomeration, electrostatic charging or a relatively high percentage of particles smaller than 100  $\mu\text{m}$ , wet sieving becomes the appropriate method.

This method is recommended for RDX, PETN and HNS.

Other methods which work without separation of the classes of particle size are LALLS and photometric determination of particle size distribution. They can be used for characterization of particle distribution of all ingredients. According to the related ingredient STANAGs LALLS has to be used with aluminium and red phosphorus.

The interpretation of results of LALLS are based on the assumption of a certain particle shape. Therefore the results of LALLS are not comparable to sieve analysis. Particle size distribution from this method is always linked to measurement conditions, which have to be specified clearly.

Photometric determination is also regarded as a suitable alternative to sieve analysis.

## 2.4.1 Dry Sieving

### Principle

Particles are sorted into categories solely on the basis of their sizes. The sieves are stacked on top of each other, with the sieve containing the coarsest openings on top. This set of sieves is vibrated until the residue on each sieve can pass through the upper sieve and cannot pass through the lower sieve. The residue on each sieve is weighed.

### Applicability

This procedure is applicable for AN.

### Apparatus

- sieving machine
- sieves (in the individual STANAGs details are given which aperture(s) to be taken for the various classes of particle sizes)
- spatula
- analytical balance

### Reagents

- carbon black to avoid adhesion and caking. Alternatively tricalcium phosphate may also be used. Approximately up to 1% might be added.

### Procedure

Weigh each empty sieve ( $w_{1i}$ ), where  $i = 1, 2, \dots, n$ , for a stack of  $n$  sieves, including the pan at the bottom of the stack. Stack the sieves on top of each other, with the sieve containing the coarsest openings on top. Tare this set of sieves and add approx. 30 g of the specimen weighed to the nearest 0.1 g ( $w_2$ ). Put the sieves on the sieving machine, fix them and start the vibration program. Release the sieves when this program is finished and reweigh the sieves ( $w_{3i}$ ).

### Reporting

Calculate the total mass of the sample recovered,  $w_4$ , as follows, and check if the difference between  $w_2$  and  $w_4$  lies within the limits of precision of weighing:

$$w_4 = \sum_{i=1}^n (w_{3i} - w_{1i}) \quad (\text{eq. 2.4.1.1})$$

$w_{1i}$  [g]: weight of empty  $i^{\text{th}}$  sieve.

$w_{3i}$  [g]: weight of  $i^{\text{th}}$  sieve (and residue) after sieving.

For each sieve, the percentage of the sample retained on the sieve will be reported, together with the sieve opening size, as:

$$\% \text{retained on } i^{\text{th}} \text{ sieve } (m_i) = \frac{(w_{3i} - w_{1i})}{w_4} \times 100\% \quad (\text{eq. 2.4.1.2})$$

$m_i$  is the size of the openings in the  $i^{\text{th}}$  sieve in micrometers.

#### Precision:

Amount of sample and accuracy of weighing have to be chosen to ensure the verification of the specification to be fulfilled.

The requirements can be checked by simple simulations with a spreadsheet:

Step 1: define the range of percentage of a sample retaining on each sieve according to the specification.

Step 2: anticipate a certain percentage retaining on each sieve by use of the randomize-function.

Step 3: determine the range of weight for each sieve according to the anticipated accuracy of the weighing procedure.

Step 4: check if the resulting range of percentage still is within the specified limits

If the percentage of results which lie outside the specification exceeds a certain level (eg. 10%), a higher amount of sample and/or a balance with better accuracy have to be used.

#### **To give an example:**

The specification for granulation of RDX, Class 6, gives the following definition:

Mesh size [ $\mu\text{m}$ ]	Weight Percent Nominal	Weight Percent Maximum	Weight Percent Minimum
250	99	100	96
180	97	100	91
125	83	93	67
90	65	80	43
63	36	50	22
45	22	36	8

With a 50 g sample and a series of 50 randomly generated sets of actual percentage between Max- and Min-values of the sample retained on each sieve, the weighing results will be within the specified range with a score of 30% if the accuracy of the balance is 0.1 g, which certainly would be unacceptable. If the accuracy of the balance is 0.01 g, the score will be around 95%, which is regarded as acceptable.

## 2.4.2 Wet Sieving

### Principle

Wet sieving with a set of specified sieves using water spray is used for determination of granulation.

### Applicability

This procedure is applicable for RDX, PETN and HNS.

### Apparatus

- set of sieves (e.g. with 0.800 mm, 0.600 mm, 0.500 mm, 0.315 mm, 0.200 mm, 0.180 mm, 0.150 mm, 0.106 mm and 0.075 mm aperture), with diameters of at least 150 mm;
- analytical balance  $\pm 0.1$  mg
- oven
- 600 ml beaker
- wash bottle
- fritted glass filtering crucible (coarse porosity)
- desiccator

### Reagents

- 2% solution of a wetting agent (e.g. dioctyl sodium sulfosuccinate).
- anhydrous methanol

### Procedure

Weigh a  $50 \pm 0.05$  g sample of dry sample to the nearest 0.01 g. Transfer the sample to a 600 ml beaker containing approximately 300 ml of a 2% solution of a suitable wetting agent, such as dioctyl sodium sulfosuccinate. With the aid of a rubber policeman attached to a glass stirring rod, stir the mixture for a few minutes wetting the sample thoroughly and breaking up as many of the aggregates as possible.

Using a spray nozzle under tap water pressure, quantitatively transfer this mixture to the uppermost sieve of the set of sieves, the largest mesh being placed on top. This assembly should be set up near a water tap and drain. Provision should be made to prevent transfer of the explosive to the drain. Adjust the pressure of the spray so that when the spray strikes the sample at an angle approximately perpendicular to the screen from a height of 50-75 mm, it is possible to wash the sample back and forth across the sieve without splashing any of the material over the side of the sieve. The spray should be moved about the screen at a rate such that the spray would traverse the diameter of the screen 1 to 2 times per second. Gently crush the wet agglomerates on the top sieve with the aid of a rubber policeman and continue washing the material back and forth across the sieve with the water spray until all the agglomerates have been broken and only individual crystals larger than the mesh of the sieve remain on the sieve. The rubber policeman shall be used in breaking up the agglomerates only on the uppermost sieve. Remove the top sieve, add a few drops of a 10% solution of the wetting agent to the material on the next sieve, and wash until no change is noticed in the amount of material remaining on the sieve. Repeat this procedure for each of the sieves.

After the washing has been completed, transfer quantitatively by means of a suitable transfer funnel the portions remaining on each of the screens into a separate previously-tared fritted glass filtering crucible of coarse porosity as follows: Hold the screen in an almost vertical position and with a moderate spray of water from the spray nozzle, gently wash the material to the lower part of the screen by drawing the spray back and forth across the screen, beginning at the top and moving slowly down the screen as the crystals move down. When the material has been collected at the lower part of the sieve, it can readily be washed into the crucible with a stream of water from a wash bottle.

Aspirate the crucible during the transfer process and for approximately 2 minutes after the transfer has been completed. Turn off the suction and add 15 ml of anhydrous methanol to the crucible and contents; allow the methanol to remain in contact with the explosive for approximately 5 seconds and then remove it with the aid of suction. Wash the contents of the crucible once more with anhydrous methanol as described above and then aspirate the crucible and contents until the odor of methanol is no longer discernible. Dry the crucible and contents for 15 minutes in an oven maintained at  $105 \pm 2^\circ\text{C}$ , cool them in a desiccator, then weigh the crucible and its contents.

#### Expression of the Results

Determine the weight of material retained on each sieve ( $w_i$ ) and calculate the percentage passing through each sieve on the basis of the dry weight of the sample ( $W$ ).

$$\% \text{ passing sieve } s_i = \frac{\left( W - \sum_{i=1}^n w_i \right)}{W} * 100\% \quad (\text{eq. 2.4.2.1})$$



### Precision

See comments 2.4.1

## **2.4.3 LOW ANGLE LASER LIGHT SCATTERING (LALLS)**

### Principle

„LALLS“ means Low angle laser light scattering. Particles in a suspension cause scattering of a focussed laser beam. The angle of scattering depends on the size of the particle as well as the shape. **The results are therefore dependent on certain assumptions concerning shape and size. Therefore the LALLS method will not give identical results to the sieving methods.**

### Applicability

This procedure is mandatory for RDX, PETN and AN, but it can be used for most explosive powders, such as HMX, CI-20, NTO, etc.

### Apparatus

- LALLS spectrometer including cell and dispersion unit; spatula

### Reagents

- dispersant (solvent in which explosive sample is insoluble), eventually also a surfactant can be advantageous

### Procedure

Choose optics according to the particle size distribution expected. Place the dispersant in the dispersion unit and let it circulate. Perform alignment and measuring of background. Take the spatula and fill small portions of the specimen into the dispersion unit. The obscuration shall be between 0.1 and 0.3. Start measurement of the sample.

### Reporting

The software of the spectrometer calculates the particle size distribution from the distribution of the laser light intensity measured. It is possible to determine the number distribution, the length distribution, the surface distribution and the volume distribution. The result should be reported as volume distribution. The type of LALLS spectrometer, the dispersant, the optics and the velocity of the stirrer of the dispersion unit must be reported.

Precision

Uncertainty of the measurement is mainly governed by the dispersion process, which introduces a systematic error, if the dispersion process is not suited to the material. The random part of the uncertainty, which is attributed to precision, is of minor importance for this method.

## 2.5 SPECIFIC SURFACE

### 2.5.1 The BRUNAUER-EMMETT-TELLER Analysis (BET – Analysis)

#### Principle

The surface area is determined by BET analysis (BET = Brunauer, Emmett, Teller), which is based on the assumption, that gases are primarily absorbed in a monomolecular layer. With this method the volume of the adsorbed nitrogen at 77 K is determined.

#### Apparatus

- nitrogen adsorption instrument;
- balance

#### Reagents

- liquid nitrogen
- nitrogen gas
- helium gas

#### Procedure

NQ/HNS must be dried in a vacuum oven at around 70°C for 24 hours prior to analysis.

A clean, dry, and closed sample tube is weighed accurately. A sample of the dried NQ or HNS is introduced into this tube. The sample size depends on the specific adsorption instrument; a typical sample size is 1 to 5 g. The sample is outgassed according to the Instruction Manual of the specific nitrogen adsorption instrument for 30 minutes at 120°C (NQ) or 30 minutes at 125 to 150°C (HNS). The tube with the outgassed sample is closed and weighed accurately. The weight of the outgassed NQ or HNS sample is calculated.

The nitrogen adsorption is measured at a temperature of 77 K. The procedures in the Instruction Manual of the specific nitrogen adsorption instrument shall be followed. Whenever the sample weight is asked for, the weight of the outgassed sample must be entered. At least 5 data points shall be measured at relative pressures between 0.05 and 0.15.

The nitrogen adsorption is measured in duplicate (on 2 separate samples).

### Calculations and Reporting

The specific surface area is calculated from the measured adsorption data, applying the multipoint BET method (at least 5 data points at relative pressures in the range 0.05 to 0.15) and assuming a molecular area of adsorbed nitrogen of 0.162 nm<sup>2</sup>.

When the instrument reports the B.E.T. surface area in square meters per gram of sample, this result is recalculated in square centimetres per cubic centimetre by the formula:

$$\text{BET}_{\text{cm}^3} = \text{BET}_g * 10000 * \rho \quad (\text{eq. 2.5.1.1})$$

where:

$\text{BET}_{\text{cm}^3}$  = BET surface area in [cm<sup>2</sup>/cm<sup>3</sup>]

$\text{BET}_g$  = B.E.T. surface area in [m<sup>2</sup>/g]

10000 = conversion factor

$\rho = 1.77$ , the density of NQ in [g/cm<sup>3</sup>] or

$\rho = 1.73$ , the density of HNS in [g/cm<sup>3</sup>]

Note: The BET analysis is carried out by nitrogen adsorption in the above procedure. It may be carried out with argon adsorption as well. The temperature of measurement with argon has to be 87 K and the assumed molecular area of adsorbed argon is 0.138 nm<sup>2</sup>.

### Precision

The precision is depending on the size of the specific surface. In the range of some m<sup>2</sup>/g an overall uncertainty not less than 5% should be achieved.

<b>CHAPTER 3    GENERAL WET CHEMISTRY</b>
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### **3.1    ACIDITY AND ALKALINITY**

#### **3.1.1    Titration of Solution in Suitable Solvent, With or Without Pre-acidification**

##### General

This paragraph describes a single universal acidity-alkalinity procedure. Titration is conducted of a solution in a suitable solvent with or without pre-acidification by a certain amount of sulfuric acid. Acetone-soluble ingredients are dissolved in acetone solution and precipitated with water. Water-soluble ingredients are dissolved in water. End-point detection can be done alternatively by indicator or potentiometry.

##### Principle

Acidity or alkalinity of the sample is determined in a single back-titration by sodium hydroxide solution of a known quantity of excess sulfuric acid, with end-point detected either by indicator or by pH electrode. Titration is always conducted in relation to a blank, treated the same way.

##### Applicability

Standard procedure can be applied for acidity and alkalinity determination of CE, RDX, PETN, AN, TNT, NQ, HNS and HMX. Modifications for BuNENA and TEGDN are described in the table.

Acidity of CL-20 and NTO is determined by titration with TBAH in non-aqueous solution.

Acidity of GUDN is determined by measuring pH-Value in a solution of defined concentration.

##### Equipment

- graduated cylinders, pipette, semi-micro burette (readability of 0.01ml) and beaker of appropriate volumes;
- pH meter with appropriate connectors (optional);
- combination pH electrode (optional).

##### Reagents

- acetone (or other solvent, if required), analytical reagent quality;
- sodium hydroxide solution with concentration approximately 0.02 M, standardized before use against suitable standard (e.g. oxalic acid dihydrate);
- sulfuric acid solution with concentration approximately 0.01 M, standardized before use against suitable standard (e.g. sodium hydrogen carbonate);
- sodium carbonate with concentration approximately 0.01 M, standardized before use against suitable standard
- methyl red/methylene blue indicator (0.1 g of methyl red and 0.05 g of methylene blue in 100 ml of 95% ethyl alcohol);
- bromocresol green indicator (for BuNENA only);
- bromothymol blue indicator (for TEGDN only)
- distilled water;
- electrode filling solution (optional);
- two or more buffers at known pH (optional).

### Procedure

Dissolve  $10 \pm 0.01$  g of sample in specified volume of solvent in a 500 ml extraction flask. Shake by hand from time to time until the sample is completely dissolved. When required to assist dissolution, heat over a water bath with small condenser in the neck of the flask or use an ultrasonic bath. Cool down to room temperature before starting titration.

A special sample preparation procedure is applied for HNS.  $5 \pm 0.01$  g of sample is put into suitable ceramic mortar, 20 ml of distilled water is added and the slurry is grinded with a pestle until a smooth paste is obtained. Then, 20 ml of distilled water is further added. Titration is carried out directly in the mortar.

Where precipitation by water is required (see table 3.1.1.1), pour in slowly (20 to 30 seconds) specified volume of distilled water and wait until the explosive settles (about 10 minutes). Filtering is recommended.

When the addition of acid is required, add 2 ml of 0.01 M sulfuric acid, mix well and allow to stand for 1 hour.

Back-titrate the excess acid with 0.02 M sodium hydroxide solution introduced by semi-micro burette using a few drops of methyl red/methylene blue as the indicator, stirring until the indicator end-point is reached. Note the volume  $V_1$  of titrating solution used in the end-point, when the color turns from purple violet to green.

Alternatively, the titration end-point may also be determined using a pH electrode. For electrode and pH meter preparation, remove any salt deposits from exterior of sensor by rinsing with distilled water. Add the filling solution to electrode. Place electrode in the electrode holder and suspend in air to thoroughly wet the reference junction. Shake down the electrode to remove the bubbles. Connect the electrode to

pH meter. Verify the pH meter calibration with the buffers. From semi-micro burette, add the titrating solution in drops of 0.02 ml each and read the related voltage change (mV) on the instrument after each addition. Upon completion of titration, a curve is obtained by plotting volume (ml) of added titrant versus related voltage change (mV). The titration equivalence point ( $V_1$ ) is found in correspondence of the sharp voltage change, that is, precisely at the curve inflexion point. Alternatively, another curve can be obtained by plotting the volume (ml) of titrant versus the rate of voltage change (mV/ml) for each addition of titrant; in this case, the curve minimum corresponds to the equivalence point of titration ( $V_1$ ).

Carry out a blank test simultaneously under identical conditions to those of the actual determination, but without the sample. Note the volume  $V_2$  of titrating solution used.

Note: Waste solutions of high explosives in acetone should be treated with care. There is a possibility of the precipitation of sensitive crystals on long standing.

### Expression of the results

When  $V_1 < V_2$ , the sample is alkaline. Alkalinity is calculated as follows:

$$\% \text{ alkalinity} = \frac{t * c_{\text{NaOH}} * (V_2 - V_1) * M * 100 \%}{1000 * W} \quad (\text{eq. 3.1.1.1})$$

$V_1$	=	volume (ml) of titrating solution used for the sample
$V_2$	=	volume (ml) of titrating solution used for the blank test
$c_{\text{NaOH}}$	=	concentration (M) of titrating sodium hydroxide solution
$W$	=	weight of sample (g)
$M$	=	equivalent molecular weight of a compound which is used for expression of alkalinity (106/2 = 53 g/mole for $\text{Na}_2\text{CO}_3$ , 40 g/mole for NaOH)
1000	=	conversion factor from litres to millilitres
$t$	=	titer

When  $V_1 > V_2$ , the sample is acidic. The acidity of the sample is given by:

$$\% \text{ acidity} = \frac{t * c_{\text{NaOH}} * (V_1 - V_2) * M * 100 \%}{1000 * W} \quad (\text{eq. 3.1.1.2})$$

where: (other symbols see above)

$M$  = equivalent molecular weight of a compound which is used for expression of acidity (98/2 = 49 g/mole for  $\text{H}_2\text{SO}_4$ , 63 g/mole for  $\text{HNO}_3$ , 60 g/mole for  $\text{CH}_3\text{COOH}$ );

Determination of titer**0.02 N NaOH:**

80 mg of Potassium hydrogen phthalate (molecular weight: 204.224 g/mole), which has been dried to constant weight at 110°C before, is weighed to the nearest 0.1 mg ( $w_1$ ) in a 150 ml beaker and dissolved in 80 ml distilled water.

The solution is titrated with phenolphthalein as indicator and the volume (ml) needed is noted ( $V_1$ ). Approximately 20 ml of a 0.02 N NaOH are needed.

A blank of 80ml distilled water is titrated the same way and the volume (ml) needed is noted ( $V_2$ )

The titer of the NaOH-solution is calculated as

$$t_{\text{NaOH}} = W_1 / 204.224 / (V_1 - V_2) / C_{\text{NaOH}} \quad (\text{eq. 3.1.1.3})$$

where  $C_{\text{NaOH}}$  (M) is the nominal concentration of the NaOH-Titrator

**0.1 N H<sub>2</sub>SO<sub>4</sub>:**

The titer is determined by titration of exactly 10 ml of NaOH of known titer (approx. 0.02 N), diluted to 50 ml with distilled water and using phenolphthalein as indicator. The volume (ml) is noted ( $V_1$ )

A blank of 50 ml distilled water is titrated the same way and the volume (ml) needed is noted ( $V_2$ )

$$t_{\text{H}_2\text{SO}_4} = 20 * t_{\text{NaOH}} / (V_1 - V_2) \quad (\text{eq. 3.1.1.4})$$

**Other titrators:**

Other titrators have to be calibrated following the procedure of 0.01 N H<sub>2</sub>SO<sub>4</sub> by proper adoption.

Table 3.1.1.1 Specifics for acidity / alkalinity titration of different ingredients

Explosive and max. allowed acidity/alkalinity	Solvent	Titrator	Precipitation by distilled Water	Remarks
CE 0.005% as HNO <sub>3</sub>	50 ml Acetone	0.02 N NaOH	200 ml	No acid added; if graphitated potentiometric detection recommended
RDX 0.01-0.05% as HNO <sub>3</sub>	100 ml Acetone	0.02 N NaOH	100 ml	No acid added



(Type A) or CH <sub>3</sub> COOH (Type B)				
PETN 0.01% as HNO <sub>3</sub> or 0.01% as Na <sub>2</sub> CO <sub>3</sub>	50 ml Acetone	0.02 N NaOH	No	Acid added
AN 0.02% as HNO <sub>3</sub> Alkalinity: none	200 ml dist. water	0.02 N NaOH or 0.01N H <sub>2</sub> SO <sub>4</sub>	No	No acid added; titration either with NaOH (if violet) or H <sub>2</sub> SO <sub>4</sub> (if green), depending on color of indicator; anti-caking agent may cause disturbance
TNT 0.005% as H <sub>2</sub> SO <sub>4</sub> Alkalinity: none	50 ml Acetone	0.01N Na <sub>2</sub> CO <sub>3</sub> or 0.01N H <sub>2</sub> SO <sub>4</sub>	150 ml	No acid added; titration either with Na <sub>2</sub> CO <sub>3</sub> (if violet) or H <sub>2</sub> SO <sub>4</sub> (if green), depending on color of indicator; older or lower quality might result in colored complexes which interfere visibility of indicator color change
HNS 0.05% as H <sub>2</sub> SO <sub>4</sub> Alkalinity: none	40 ml dist. water	0.02 N NaOH	No	No acid added
NQ 0.06% as H <sub>2</sub> SO <sub>4</sub>	200 ml water	0.05 N NaOH		80°C until completely resolved
HMX Acidity: ca. 0.0045- 0.0087% as HNO <sub>3</sub>	500 ml Acetone	0.02 N NaOH	100 ml	Warm up solvent, filtrate, titrate at room temperature; no acid added
BuNENA 0.025% as H <sub>2</sub> SO <sub>4</sub> 0.025% as Na <sub>2</sub> CO <sub>3</sub>	60 ml Acetone	0.01 N KOH in Methanol or 0.01 N HCl in Methanol	No	No acid added; titration either with Na <sub>2</sub> CO <sub>3</sub> or H <sub>2</sub> SO <sub>4</sub> , depending on color of indicator (Bromocresolgreen: 1% in methanol)
TEGDN 0.002% as H <sub>2</sub> SO <sub>4</sub> 0.002% as Na <sub>2</sub> CO <sub>3</sub>	100 ml Toluene	0.01N NaOH or 0.01N H <sub>2</sub> SO <sub>4</sub>	2x 50ml Extraction	If color at blank titration turns blue, acid is added until color turns yellow; the same amount is added to all samples; titration either with NaOH (if yellow) or H <sub>2</sub> SO <sub>4</sub> (blue/green), depending on color of indicator (Bromothymolblue: 1% in Ethanol)

For calibration of a base the H<sub>2</sub>SO<sub>4</sub>-titrator is used as a probe, and the NaOH-titrator for calibration of an acidic titrator. The volume of titrator on calibration should always be around 20 ml, to provide optimum precision.

In general a filtration of the solution is very helpful to be able to see the color change. Of course this filtration step must be made in the blank test as well.

Remarks concerning potentiometric detection:

Some experience/results with an automatic titration device, which is able to

accurately add 10 µl of acid into the sample solution, are presented in this paragraph. If strong acids are present, the method works very well. If no acids are present the accuracy of the method is much higher than the stability of the pH value of the solutions themselves. Evaporation of acetone, combined with a temperature and pH change made a stable baseline impossible. Therefore one should work in a closed volume, if possible thermostated. Then the pH of acetone slowly seems to change, because of possible reactions with water, moisture or CO<sub>2</sub>. So a solvent without acidic protons (e. g. THF, acetonitrile, dichloromethane, DMSO) instead of acetone is strongly recommended. Then the pH-electrode should not be based on water/KCl but an ethanolic LiCl electrode would be much better. If these steps are made (no evaporation, no acetone, LiCl electrode system) everything works much finer than the burette titration method which was presented above in this chapter.

### Precision

Example for Tetryl:

The requirement of max. 0.005% corresponds to an amount of 0.16ml of the titrant. As accuracy of titration is typically 0.01-0.02 ml, the precision is limited to 6-12% at this level. Minimum detectability is 0.0006% HNO<sub>3</sub>.

## 3.1.2 Titration With TBAH in Solvent System

### Principle

The dry material is dissolved in a suitable solvent system and titrated in a non-aqueous system using tetra-butylammonium hydroxide (TBAH) to determine the total acid in the sample.

### Procedure

The substance is weighed ( $w_1$  in [g]) into a suitable beaker and the specified amount of solvent is added (see table 3.1.2.1). The mixture is stirred until the explosive is dissolved completely. The solution is titrated ( $V_1$  [in ml]) using a potentiometric titrator with a TBAH solution of the specified normality (see table 3.1.2.1) in a suitable solvent ( $c_1$ ).

The TBAH solution is standardized using a primary standard acid (e.g. potassium hydrogen phthalate) of a known quantity in this same apparatus. A combination glass electrode or equivalent is used for measuring. A blank is also done using the same procedure but omitting the sample ( $V_2$ ). The acidity is calculated as follows:

$$\text{Acid (meq/100 g)} = (V_1 - V_2) \cdot c_1 \cdot 100 / w_1 \quad (\text{eq. 3.1.2.1})$$

Table 3.1.2.1 Specifics for acidity / alkalinity titration of different explosives

Explosive	Amount	Solvent	Titrant
NTO	0.1±0,001 g	100 ml IPA/H <sub>2</sub> O(97/3 V/V%)	0.1N TBAH in IPA
CL-20	5.0±0,1 g	100 ml THF	0.05N TBAH in THF

Equipment

An automatic potentiometric titrator assembly comprised of a recording potentiometer fitted with an automatic burette and equipped with a 20 ml syringe and a combination glass-Ag/AgCl electrode can be used.

Standardization of TBAH

Tetra-butylammonium hydroxide (TBAH) 0.1 N (This is a commercial solution in an isopropanol/methanol mixture. This solution must be stored between 16 and 24°C.).

- solvent for method
- benzoic acid, analytical grade, dried at 65.5°C.

The temperature of the TBAH solution should not vary by more than ±1°C during the determination of the TBAH titer and the determination of acidity of the explosive.

Determination of TBAH Titer.

Transfer a weighed portion of approximately 0.1 gram of benzoic acid (weighed to ± 0.1 mg) to a 150 ml beaker. Add 100 ml of the solvent. Stir until completely dissolved. Then, using the potentiometric titrator, titrate with the TBAH 0.1 N solution. A minimum of three tests with benzoic acid and three tests without benzoic acid (blank tests) shall be conducted. The titrator determines the equivalence point, which is the point where the addition of a minimum amount of TBAH titration solution leads to a maximum change in potential.

The normality of TBAH is calculated as follows:

$$\text{Normality of TBAH} = 1000 \cdot m \cdot 122.1 \cdot (V1 - V0) \quad (\text{eq. 3.1.2.2})$$

m: weight of benzoic acid used [g]

V1: Volume of TBAH solution used to reach the equivalence point in the benzoic acid test. The average of three tests is used [ml].

V0: Volume of TBAH solution used to reach the equivalence point for the blank test. The average of three tests is used [ml].

122.1: Molecular weight of TBAH [g/mole]

### 3.1.3 Determination of pH-Value of a Defined Solution With pH-Electrode

#### Principle

The acidity of GUDN is determined by measuring the pH-value of a 0.2% solution.

(A pH-value <4.0 is corresponding to an acid content >0.005% H<sub>2</sub>SO<sub>4</sub>). Acid-base titration is not recommended as a method since GUDN as an acid in itself would interfere with the titration of acidic impurities.

#### Equipment

pH-meter with pH-electrode with a 2 decimal resolution.

#### Procedure

Weigh 0.10 g of a GUDN sample into a 50 ml volumetric flask and fill up to the mark with previously boiled and cooled distilled water. Let the flask with sample stand in an ultrasound bath until all GUDN has been dissolved.

Transfer about 20 ml to a glass beaker and add a magnetic stirrer. Start the stirrer and measure the pH-value with a calibrated pH-meter.

Report the result with 1 decimal.

## 3.2 MOISTURE

### 3.2.1 Karl Fischer Titration (Coulometric Procedure)

#### Principle

The explosive is dissolved in dried methanol. Its moisture content is titrated according to Karl Fischer (dead stop procedure).

#### Apparatus

- Karl Fischer titrator
- 100 ml beaker
- micro syringe
- analytical balance

#### Reagents

- Karl Fischer solution
- disodium tartrate dihydrate analytical reagent grade
- methanol analytical reagent grade, dried
- toluene analytical reagent grade, dried
- pyridine analytical reagent grade, dried

#### Procedure

For different ingredients, different sample masses and methanol amounts are recommended. They are listed in the following table.

**Table 3.2.1.1** Specifics of sample preparation for Karl Fischer titration

Explosive	Sample mass	Solvent
AN	6 g	50 ml of methanol
TNT	8-10 g	100 ml of a 1:1 mixture of toluene and methanol
AP	5 g	50 ml methanol
BuNENA	7 ml	50 ml of methanol
TEGDN	30 µl	No solvent ; determination according to AOP4719

Weigh the explosive to the nearest 0.0001 g (w) into a well-dried 100 ml beaker and close it tightly immediately after weighing [BuNENA: Use a disposable syringe to

extract about 7 ml BuNENA. Weigh the syringe, and add the material to the neutralized solution. Weigh the empty syringe, and calculate the sample weight]. Add the appropriate amount of solvent (see table above) and wait until all explosive is dissolved. The solution is then titrated manually until its color changes (dead stop principle). Note the amount of Karl Fischer reagent solution needed ( $V_1$ ).

Run a blank experiment with 50 ml of methanol in parallel to determine the moisture content of the solvent. Note the amount of Karl Fischer reagent solution needed ( $V_2$ ).

Determine the titer of the Karl Fischer solution by titrating a disodium tartrate dihydrate sample ( $w_T$ ), or alternatively, by directly adding a small amount (50.0 mg) of water through a micro syringe. Note the amount of Karl Fischer reagent solution needed ( $V_3$ ).

If an automatic Karl-Fischer titrator is used, put the sample into a well-dried volumetric flask (50 ml) and dilute to the mark with dried solvent. A measured aliquot is then added from the flask to the automatic titrator for titration to a 30 second end point.

Afterwards, a blank experiment with 50 ml of methanol has to be run.

### Reporting

The amount of water in the sample is calculated by

$$\% \text{ water} = \frac{T \cdot (V_1 - V_2)}{10 \cdot w} \quad (\text{eq. 3.2.1.1})$$

$v_1$  = amount of Karl Fischer solution for the sample containing solution [ml].

$v_2$  = amount of Karl Fischer solution needed for the blank solution [ml].

T = titer of the Karl Fischer solution (tested by disodium tartrate dihydrate) [mg water/ml reagent].

w = weight of the sample specimen [g].

$$T = \frac{w_T \cdot 0,156}{V_3 - V_2} \quad (\text{eq. 3.2.1.2})$$

### Precision

For a sample of 7 g of BuNENA a maximum content of approximately 3.5 mg water is tolerated. If the titer of the Karl Fischer solution is 1ml/mg water and the volumetric resolution is 1 drop (50  $\mu$ L), the precision for determination of this amount is 1.5% at best.

### **3.2.2 Karl Fischer Titration (Volumetric Procedure)**

### Apparatus

Karl Fischer titrator with magnetic stirrer.

### Reagents

- Karl Fischer reagent
- methanol, p.a. or absolute grade

### Procedure

At least weekly, or when refilling the reservoir, standardize the Karl Fischer reagent with a known amount of deionised water added under the surface of the conditioned solvent; repeat the test until checks agree within 0.03 mg/ml. Fill the sample cup with about 50 ml methanol and titrate to equilibrium. Weigh the explosive to the nearest 0.0001 g (w) into a well-dried 100 ml beaker and close it tightly immediately after weighing [BuNENA: Use a disposable syringe to extract about 7 ml BuNENA. Weigh the syringe, and add the material to the neutralized solution. Weigh the empty syringe, and calculate the sample weight]. The sample is titrated until equilibrium is reached. The water content is calculated from the volume of reagent used and the water equivalent (WE) of the reagent:

### Calculation

$$\% H_2O = \frac{vol * WE}{10 * M} \quad (\text{eq. 3.2.2.1})$$

vol = volume of KF reagent used [ml]

WE = The water equivalent of the reagent [mg H<sub>2</sub>O/ml]

M = Weight of sample [g]

### Precision

See 3.2.1

### 3.3 TOTAL VOLATILES

#### 3.3.1 Total Volatiles: Determination by Heating and Reweighing

##### Principle

This method is used for the determination of volatile impurities in the sample by simple heating and reweighing. Different explosives require different temperatures and heating times. They are collected in the following table.

Table 3.3.1.1 Applicability of procedures for the determination of total volatiles

Ingredient	Current procedure	Comments / remarks
CE	20 g sample at 100°C for 2 hours;	
AN	10 g sample at 70°C for 5 hours	
NQ	5 g sample at 100°C for 2 hours	
HNS	5 g sample at 100°C for 2 hours	in vacuum (typically approx. 10 mbar)
AI	5 g sample at 105°C for 2 hours	ageing in dry nitrogen stream
NTO	5 g sample at 103°C for 2 hours	
GUDN	4 g sample at 110°C for 2 hours	

##### Apparatus

- oven, drying cabinet, vacuum oven (see table above)
- balance
- petri dish or beaker

##### Procedure

A sample of about 5 to 20 g (see above table for required amount) is put on a tared petri dish and its weight is determined to the nearest 0.001 g. The petri dish with material is dried for several hours (see above table for required time) in an oven at conditions specified in table 3.3.1.1 and cooled down in a desiccator. The weight after drying is determined. Samples are analyzed till constant weight within limit of precision after consecutive steps of additional heating for 60 minutes.



Reporting

Calculate the quantity of volatile matter as follows:

$$\text{Volatile matter [\%]} = 100 * \frac{W_2 - W_1}{W} \quad (\text{eq. 3.3.1.1})$$

W = weight of sample [g],

W<sub>1</sub> = weight of petri dish with sample after drying procedure [g],

W<sub>2</sub> = weight of petri dish with sample before drying procedure [g].

Precision

Example Tetryl: the requirement of 0.1% corresponds to an amount of 20 mg volatile matter. As the procedure claims accuracy of 1 mg on weighing, the precision is limited by 5%.

**3.3.2 Total Volatiles: Determination by Applying Vacuum and Reweighing**Principle

This method is used for determination of volatiles in red phosphorous by maintaining a low pressure for 24 hours.

Apparatus

- desiccator
- vacuum pump, providing pressure below 1333 Pa.
- balance with an accuracy of 0.1 mg

Procedure

Transfer 5 g ( $\pm 0.05$  g) of the sample to a clean, dry, aluminium dish with a loosely fitting lid, and weigh ( $m_1$ ) to the nearest 1 mg. Carefully remove the lid and place the dish, with the lid alongside, in a vacuum desiccator over freshly activated silica gel. Evacuate the desiccator and leave for 24 hours, during which time the pressure in the desiccator must not exceed 10 mm mercury (1333 Pa). Release the vacuum carefully, passing the incoming air through a suitable drying vessel filled with activated silica gel. Replace the lid on the dish and reweigh ( $m_2$ ).

NOTE: It is important not to disturb the very light amorphous powder when releasing the vacuum.

#### Reporting

$$\text{Volatile matter}(\%) = 100 \frac{(m_1 - m_2)}{5} \quad (\text{eq. 3.3.2.1})$$

#### Precision

If the weight is determined with an accuracy of 1 mg, the precision at the maximum allowed content of 0.5%, which corresponds to 25 mg, is 4%rel.

### 3.4 INSOLUBLE IMPURITIES

#### 3.4.1 Insoluble Impurities: Determination by Dissolving and Reweighing of Filtered Insoluble Material

##### Principle

This method is used for the determination of insoluble impurities in the sample by dissolving the explosive in an appropriate solvent, filtering the insoluble material off and reweighing the crucible after drying. Different explosives require different solvents. They are collected in the following table.

Table 3.4.1.1 Applicability of procedures for the determination of insoluble impurities

Ingredient	procedure	Sample amount	Solvent used	Reaction time	Remarks
CE	Solution	10 g	200 ml of acetone at room temp.	Until dissolution is complete	
RDX	Solution	10 g	250 ml of acetone on a steam bath	Until dissolution is complete	
PETN	Solution	10 g	250 ml of acetone on a steam bath	Until dissolution is complete	
AN	Solution	10 g	25 ml of water (20 ± 5°C)	Not specified	
TNT	Solution	10 g	150 ml of dry warm toluene	30 min	
NQ	Solution	50 g	2000 ml of boiling distilled water	Not specified	
HNS	Solution	5 g	25 ml of boiling DMF	1 min	

Table 3.4.1.1 (continued) Applicability of procedures for the determination of insoluble impurities

Ingredient	procedure	Sample amount	Solvent used	Reaction time	Remarks
HMX	Solution	10 g	50 ml of DMSO (water bath)	Not specified	
AP	Solution	25 g	175 ml of water	Not specified	
AI	Solution	10 g	50 ml of water + HCl	Until dissolution is complete	
CL20	Solution	10 g	100 ml of acetone	15 min	drying at max. 60°C
GUDN	Solution	10g	20 ml DMSO	Heat on water-bath until dissolution is complete	washing of residue with acetone

#### Apparatus

- 250 ml graduated cylinder
- hot plate or steam bath
- tared Gooch D3, or, alternatively, a tared sintered glass crucible with equivalent porosity
- water bath
- oven
- CaCl<sub>2</sub> containing desiccator
- analytical balance capable of measuring to 0.001 g

#### Reagents

- different solvents, see table 3.4.1.1, each in reagent grade

#### Procedure

The crucible used for filtration has to be pretreated by heating to 700±20°C for 1 hour and subsequent cooling in a desiccator.

Take the necessary amount of the sample (W), and place it in a beaker of appropriate size. Add the necessary amount of solvent, cover with a watch glass, and leave the beaker until dissolution is complete. If higher temperatures are necessary (see table above), use steam or oil baths. Stir occasionally to assist solution, and then leave the beaker on the bath to coagulate the insoluble matter. Also speeding up of the process by ultrasonic bath could be appropriate. At the end of this period of

time (at least 30 minutes) pour the cooled down solution through a previously prepared and weighed ( $W_1$ ) filtering crucible of porosity grade G3 or the equivalent. Wash the residue with the solvent, and continue washing until the residue is free from explosive.

This can be tested by pouring a small amount of the washing on a watch glass. The washing procedure is complete if there are no visible traces remaining after vaporization of the solvent.

Dry the crucible and contents at 100°C until a constant weight is obtained, cool in a desiccator, and weigh ( $W_2$ ).

#### Calculation

$$\text{insol. matter}(\%) = \frac{(W_2 - W_1)}{W} * 100 \quad (\text{eq. 3.4.1.1})$$

#### Precision

Example TNT: maximum tolerable impurities are 0.05%

With 10 g TNT, this corresponds to 5 mg TNT; with an anticipated accuracy of 1 mg, this results in a precision of 20%rel.

### **3.4.2 Insoluble Impurities in Aqua Regia : Procedure for Red Phosphorus**

#### Apparatus

- sieve (ISO 3310-1; BS410) 50 mm diameter and of the following aperture size: 250  $\mu\text{m}$
- analytical balance capable of measuring to 0.001 g
- watch glass
- beaker 600 ml

#### Reagent

- aqua regia: mix together carefully, 1 volume of nitric acid ( $d = 1.42 \text{ g/ml}$ ) and 3 volumes of hydrochloric acid ( $d = 1.18 \text{ g/ml}$ )

#### Procedure

Transfer 5 ( $\pm 0.05 \text{ g}$ ) of sample to a 600 ml beaker and add 50 ml water and 20 ml of aqua regia. Cover the beaker with a clock glass. Warm to initiate the reaction, then

remove from the heat and add a further 20 ml of aqua regia. Maintain the reaction by the application of heat and dropwise addition of the aqua regia until a total of 120 ml of the reagent has been added. When the vigorous reaction has subsided, heat the solution to boiling and boil for 5 minutes. Cool to ambient temperature and dilute the solution to approximately 300 ml with water.

Filter the solution through a No 42 filter paper and transfer any residue in the beaker quantitatively to the paper. Wash the filter paper thoroughly with water and finally with acetone. Place the filter paper in a previously ignited, cooled and weighed porcelain crucible ( $m_1$ ) and dry in an oven at  $103 \pm 2$  °C. Ignite the crucible and contents at  $700 \pm 20$  °C until all of the carbon has been burnt off, cool and reweigh ( $m_2$ ).

Transfer the residue in the crucible to a 250  $\mu\text{m}$  sieve and brush with a soft brush until no more material passes the sieve. Weigh any material retained on the sieve ( $m_3$ ).

### Calculation

$$\text{Total material insoluble in aqua regia (\%)} = 100 (m_2 - m_1) / 5 \quad (\text{eq. 3.4.2.1})$$

$$\text{Matter insoluble in aqua regia retained on a 250 } \mu\text{m} \text{ sieve (\%)} = 100 m_3 / 5 \quad (\text{eq. 3.4.2.2})$$

### Precision

With the maximum allowed quantity of 0.1% and an accuracy of the balance of 1mg, this corresponds to a precision of 20%rel.

## **3.5 SOLUBLE IMPURITIES**

### **3.5.1 Determination of Matter Soluble in Diethyl Ether by Soxhlet Extraction**

#### Principle

Soxhlet extraction procedures extract soluble impurities within another substance. It should be stated that a sample pre-treatment (especially lowering particle sizes) may be necessary. Table 3.5.1.1 shows the applicability of this test and the solvents to be used.

#### Apparatus

- 400 ml flask
- desiccator
- Soxhlet extractor

- water bath
- oven
- analytical balance, accuracy 0.1 mg

### Reagents

- diethyl ether, reagent grade

### Procedure

Dry a clean 400 ml flask in an oven at 90°C, and cool in a desiccator to constant weight. Weigh 10 g (25 g) of the explosive to the nearest 0.1 mg and record as  $W_1$  and extract for 4 hours with 100 ml (150 ml) of diethyl ether using a Soxhlet extraction apparatus with a Whatman single thickness, fat-free extraction thimble or equivalent. After extraction has been completed, evaporate the diethyl ether almost to dryness using a boiling water bath. Dry residue in an oven at 90°C to a constant weight and then cool in a desiccator. Weigh and record this as  $W_2$ . Run a blank with each group of the tests and record this as  $W_3$ . Calculate the following quantity:

$$\text{Percent Matter Soluble} = \frac{((W_2 - W_1) - W_3) * 100}{\text{weight of sample}} \quad (\text{eq. 3.5.1.1})$$

NOTE. Diethyl ether is flammable, and appropriate safety precautions against accidental ignition must be taken. Furthermore peroxides contained in ether can constitute an explosive hazard.

### Precision

Example AP: Given a maximum of 0.01%, this corresponds to 2.5mg; with the accuracy of the balance of 0.1mg, the precision is determined as 4%.

Table 3.5.1.1. Procedures applicable for the determination of soluble impurities

Ingredient	procedure	Sample amount	Solvent used	Solvent amount	Reaction time
AN	Soxhlet extraction	10 g	ether	150 ml	5 h
AP	Soxhlet extraction	25 g	ether	100 ml	2 h
AI	Soxhlet extraction	10 g	ether	100 ml	4 h

### 3.5.2 Determination of Water Soluble Material

#### Principle

The explosive is washed several times with water. All water-soluble impurities are dissolved and by reweighing the explosive after drying, the quantity of water-soluble material is determined.

#### Apparatus

- 100 millilitre (ml) tall form beaker
- desiccator
- vacuum oven
- sintered-glass crucible
- oven
- analytical balance, accuracy 0.1mg

#### Reagents

- water, reagent grade with 5 volume percent of reagent grade methanol added

#### Sample preparation and procedure

A 5-gram sample of explosive, which has been heated at  $100 \pm 5^\circ\text{C}$  for 2 hours and stored in a desiccator afterwards, weighed to nearest 0.1 mg ( $W_1$ ), is placed in a vitreous 100 millilitre (ml) tall form beaker. The sample is washed three times by decantation. Use 40 ml of water containing 5 volume percent of methanol for each wash. Allow the sample to remain in contact with the water-methanol for 20 minutes. Stir the sample with a flat tipped stirring rod to aid in wetting the particles and break

up lumps. All of the wash solution is filtered through a tared ( $W_c$ ) 50 ml medium porosity, high form, sintered-glass crucible, which has been dried to constant weight at  $100 \pm 5^\circ\text{C}$  before. After the sample has been quantitatively transferred to the crucible with water-methanol, it is dried to constant weight at  $100 \pm 5^\circ\text{C}$ , cooled, and weighed ( $W_2$ ). The loss in weight is reported as water-soluble material.

### Calculation

$$\text{Percent Matter Soluble} = (W_1 - (W_2 - W_c)) * 100 / W_1 \quad (\text{eq. 3.5.2.1})$$

## 3.6 INORGANIC MATTER (ASH)

**Table 3.6.1** Applicability of different procedures for the determination of inorganic matter (ash)

Ingredient	procedure	Sample amount
CE	3.6.1	10 g
RDX	3.6.1	10 g
TNT	3.6.2	5 g
NQ	3.6.2	5 g
HNS	3.6.2	5 g
HMX	3.6.1	10 g
AP	3.6.2	5 g

### 3.6.1 Determination of Ash by Incineration in Crucible

This test is required when the amount of acetone insoluble matter from the acetone insoluble determination is greater than 0.03%. Remove any organic matter by heating the material collected in the crucible in Procedure 3.4.1 to  $700 \pm 20^\circ\text{C}$ . Cool the crucible and reweigh it to the nearest 0.1 mg ( $w_3$ ). Calculate percentage of inorganic insoluble material using the equation below.

$$\% \text{ Inorganic matter} = \frac{(w_3 - w_2)}{w_1} \times 100\% \quad (\text{eq. 3.6.1.1})$$

where  $w_1$  = weight of the sample

$w_2$  = weight of the empty crucible

$w_3$  = weight of the crucible after re-heating



### 3.6.2 Determination of Sulfated Ash

#### Principle

The dry material is warmed gently with sulfuric acid and then heated more strongly to burn off the organic matter. The reaction is very vigorous and great care should be exercised. The reaction must be carried out behind a suitable safety screen and protective goggles and gloves must be worn.

#### Apparatus

- muffle furnace
- desiccator
- 100 mm diameter silica dish

#### Reagents

- concentrated sulfuric acid (18 M)

#### Procedure

Heat a clean 100 mm diameter silica dish in a muffle furnace at 700°C for 30 minutes. Cool in a desiccator for 45 minutes and weigh accurately ( $W_1$ ). Transfer  $5 \pm 0.1$  g of the dry material into the dish and carefully add 10 ml of concentrated sulfuric acid (18 M) so that it is evenly distributed over the surface of the sample.

Warm the dish and contents on a steam bath for 30 minutes to ensure that the sample is completely wetted by the acid. With a Bunsen flame, gently apply heat to the dish held on a clay triangle until the sample begins to char. Remove the flame and allow the reaction to proceed unaided. As the reaction subsides, apply sufficient heat to sustain the reaction until all the sample has charred. Continue heating gently until no more sulfuric acid fumes are evolved. Heat the dish to dull red until all residual carbon has been burned off. Place in the muffle furnace at 700°C for 30 minutes. Cool the dish in a desiccator for 45 minutes and reweigh ( $W_2$ ).

#### Calculation and Reporting

Calculate the sulfated ash content and report as a percentage by weight of the sample.

$$\text{Percentage sulfated ash} = 100 * (W_2 - W_1) / 5 \quad (\text{eq. 3.6.2.1})$$

### 3.7 GRITTY PARTICLES

#### Definition of grit

Gritty particles are hard and sharp-edged inorganic particles of a size of at least 63  $\mu\text{m}$ . They may lead to a higher sensitivity of the energetic material to external stimuli (hot spot generation). Gritty particles are not necessarily insoluble in hot acids, hot bases or aqua regia.

Table 3.7.1 Applicability of different procedures for the determination of gritty particles

<b>Ingredient</b>	<b>procedure</b>	<b>Sample amount</b>	<b>Solvent used</b>	<b>Comments</b>
CE	3.7.1	50 g	acetone, 100 ml	
RDX	3.7.1	50 g	acetone, 400 ml	
PETN	3.7.1	50 g	acetone, 200 ml	Use a steam bath
TNT	3.7.1	50 g	acetone, 100 ml	
NQ	3.7.2	50 g	Boiling water, 2000 ml	Filtration over crucible, finally transfer to sieve
HNS	3.7.1	50 g	DMSO, 200 ml	
HMX	3.7.1	50 g	DMSO, 200 ml	
AP	3.7.2	50 g	Boiling water, 200 ml (repeatedly)	Filtration over crucible, finally transfer to sieve
Al	3.7.2	10 g	Aqua regia, 5 ml	Boiling for 5 minutes, neutralisation with NaOH Filtration over crucible, finally transfer to sieve
GUDN	3.7.1	10 g	DMSO, 20 ml	Use a steam bath

### 3.7.1 Determination of Grit by Direct Extraction on a Sieve

#### Equipment

- Soxhlet apparatus or any other suitable extractor
- steam bath or any other suitable heating device
- sieves with 0.25 mm (US No. 60) and 0.42 mm (US No. 40) aperture
- analytical balance capable of measuring to 0.001 g

#### Reagents

- solvent, analytical reagent quality (to know which solvent to be used, refer to table 3.7.1)

#### Procedure

Transfer a sample of  $50 \pm 0.01$  g of explosive to a 0.25 mm aperture sieve. Place the sieve in a Soxhlet apparatus or any other suitable extractor. Add sufficient solvent to the flask and extract on a steam bath until all explosive is dissolved.

Remove the sieve, count and examine the remaining particles. Brush the particles on a 0.42 mm aperture sieve, count and examine any that are retained.

Note whether the particles are gritty. Gritty particles are indicated by lack of uniformity of the material and the persistence of a scratching noise when the material is pressed and rubbed on a smooth glass slide with a smooth steel spatula.

#### Expression of the results

Report the number of gritty particles retained on 0.25 mm and 0.42 mm aperture sieves, respectively in the tested sample.

NOTE: TNT and AI require the first sieve to be used to have aperture sizes of 63  $\mu$ m (8US 230 mesh), the second shall be the 250  $\mu$ m sieve.

### **3.7.2 Dissolving and Filtering Over Crucible Prior Transferring to Sieve**

#### Procedure

Transfer the required amount of sample to an appropriate beaker and treat with solvent as specified in table 3.7.1.

Then filtrate the content over a crucible, wash with acetone and dry for one hour at 100°C.

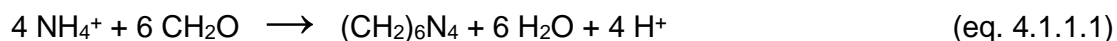
The dried residue is transferred to a 0.25mm sieve and examined for gritty particles.

Finally the residue is brushed to a 0.42mm sieve and again examined for retained grit.

<b>CHAPTER 4    SPECIFIC WET CHEMISTRY</b>
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**4.1    DETERMINATION OF AMMONIUM****4.1.1    Ammonium Content of AP and AN for Purity Control**Principle

Formaldehyde polymerizes in the presence of  $\text{NH}_4^+$  ions to urotropine according to the equation:



The hydrogen ions are titrated with alkali.

Test Apparatus

- 200 ml stoppered Erlenmeyer flask
- 50 ml burette
- pH-Meter

Reagents

- formaldehyde solution GR (min. 37 %) stabilized with 10 %  $\text{CH}_3\text{OH}$  (p.a.) 1:1 in  $\text{H}_2\text{O}$ .

Procedure

Adjust the pH of the formaldehyde solution to a value of  $\text{pH} = 8.5$  using 0.1 N sodium hydroxide.

Weigh a sample of 0.5 g (in dried condition) in an Erlenmeyer flask (w).

Add 40 ml  $\text{H}_2\text{O}$  to prepare a water solution of the sample. Add 40 ml formaldehyde solution. Stopper the flask, shake vigorously, and allow to stand for 30 minutes. The solution is then titrated with 0.1 N sodium hydroxide to a pH of 8.5 with the help of a pH-meter. A double determination is necessary and the average of the titrated volume (V) is calculated and reported.

Calculation

$$\text{Percentage } NH_4ClO_4 \text{ or } NH_4NO_3 = 100 \frac{M_w * V * N}{1000 * w} \quad (\text{eq. 4.1.1.2})$$

$M_w$  = molecular weight ( $NH_4ClO_4$  = 117.5 g/mole;  $NH_4NO_3$  = 80.04 g/mole)

$V$  = titrated volume of NaOH (mL)

$w$  = weight of sample (g)

$N$  = normality of NaOH solution (mole/L)

Precision

Example:

For a 0.5g sample of AN, the theoretical amount of 0.1N NaOH is 62.5 ml. With an accuracy of the burette of 0.05ml, this corresponds to a precision of approximately 0.1%.

**4.2 DETERMINATION OF CHLORIDE****4.2.1 Gravimetry as AgCl in AN**Principle

Dissolved chlorides react with silver ions in nitric acid conditions under precipitation of silver chloride which can be determined by gravimetry.

Apparatus

- analytical balance
- sintered glass crucible (D4) [D4 (new ISO 4793 classification P 16) describes crucibles with pore diameters of the widest pores of 10-16  $\mu\text{m}$ .]
- volumetric flask, 250 ml
- beaker, 400 ml
- pipette, 100 ml
- filtering flask with filtering attachment
- desiccator
- drying cabinet

Reagents

- distilled water, analytical reagent grade
- aqueous silver nitrate solution (0.1 M), analytical reagent grade
- nitric acid solution, 2 M, analytical reagent grade

Procedure

Perform conditioning of the crucible (storage at 120°C in the drying cabinet for 1 hour, cooling down to ambient temperature in the desiccator) and weigh it ( $w_2$ ).

Weigh a 100 g specimen of sample to the nearest 0.0001 g ( $w_1$ ) in the tared volumetric flask and dissolve it in distilled water. Fill up with distilled water to the marking. Transfer an aliquot of 100 ml into the beaker. Add some drops of nitric acid until a pH of 2 to 2.5 is reached. Add – drop by drop – a total amount of 10 ml of the silver nitrate solution. The precipitate (silver chloride) is sensitive to light. Therefore it should be filtered as soon as possible. Dry the crucible with the silver chloride precipitate under the same conditions as the crucible was conditioned. Reweigh the crucible ( $w_3$ ).

Reporting

$$\text{Ammonium chloride [\%]} = 100 * 0.3732 \frac{(w_3 - w_2)}{w_1} \quad (\text{eq. 4.2.1.1})$$

$w_1$  = Weight of the specimen [g]

$w_2$  = Weight of the empty crucible [g]

$w_3$  = Weight of the crucible and residue [g]

The factor of 0.3732 in the equation is the ratio of the molecular weights of ammonium chloride (53.49 g/mole) and silver chloride (143.32 g/mole).

Precision

With a 100g sample of AN for example, the maximum tolerated amount of ammonium chloride is 0.02% which would correspond to approximately 50mg difference of  $w_3$  and  $w_2$ . Given a 0.1mg resolution of the balance, this corresponds to a theoretical precision of 0.2%.

## 4.2.2 Titrimetry by Volhard (Excess AgNO<sub>3</sub> Retitrated by NH<sub>4</sub>SCN) in AP

### Principle

The determination is done by the Volhard Method by precipitation with an excess of silver nitrate (AgNO<sub>3</sub>) and retitration of unreacted AgNO<sub>3</sub>.

### Reagents

- 0.1 N silver nitrate
- iron (III) ammonium sulfate indicator (The indicator solution consists of a cold saturated solution of iron ammonium sulfate; for example: 200 ml H<sub>2</sub>O, 110 g salt, 10 ml HNO<sub>3</sub>)
- nitrobenzene p.a. (or reagent grade)
- 0.1 N ammonium thiocyanate (NH<sub>4</sub>SCN)
- nitric acid 65 % diluted 1:1 with water

### Test Apparatus

- beaker 250 ml
- magnetic stirrer
- 50 ml burette

### Procedure

In a 250 ml beaker, dissolve 15 g of the sample (w) in 150 ml distilled water. Under stirring, add exactly 20 ml of 0.1 N AgNO<sub>3</sub> solution. Thereafter, add 5 ml of the indicator solution, 2 ml nitrobenzene, and 5 ml HNO<sub>3</sub>.

The mixture is titrated to the endpoint (light brown) with 0.1N ammonium thiocyanate solution. A blank determination should be carried out on the equivalent amounts of reagents used in the test.

### Calculation

$$\text{Percentage Chloride as } NH_4Cl = 100 * \frac{M_w (V_A * N_A - V_B * N_B)}{w} \quad (\text{eq. 4.2.2.1})$$

V<sub>A</sub> = added amount of AgNO<sub>3</sub> solution (ml)

V<sub>B</sub> = titrated volume of NH<sub>4</sub>SCN (ml)

N<sub>A</sub> = normality of AgNO<sub>3</sub> (mmole/ml)

N<sub>B</sub> = normality of NH<sub>4</sub>SCN (mmole/l)

w = weight of sample (g)

M<sub>w</sub> = molecular weight of NH<sub>4</sub>Cl (0.05349 g/mmole)



### Precision

With a 15g sample of AN for example, the maximum tolerated amount of ammonium chloride is 0.02% which would correspond to approximately 3mg, respectively 0,056mmole, consuming 0.56mL of silver nitrate solution. Given a volumetric resolution of 50 $\mu$ L, the theoretical precision is approximately 10%.

### **4.2.3 Direct Titrimetry with AgNO<sub>3</sub> (End-point Detected by Potentiometry)**

#### Principle

The chloride content is detected by potentiometry.

#### Equipment

An automatic potentiometric titrator assembly comprised of a recording potentiometer fitted with an automatic burette and equipped with a 5 ml syringe and the following electrodes:

- Ag as working electrode
- Ag/AgCl in KCl/K<sub>2</sub>SO<sub>4</sub> as reference electrode

#### Reagents

The reagents for this test method are:

- 0.02 N AgNO<sub>3</sub> aqueous solution
- 0.3 g/l NaCl aqueous solution
- 30% concentrated HNO<sub>3</sub> (nitric acid) solution (1:1 ratio of concentrated nitric acid to water)
- distilled water

#### Procedure

Transfer a weighed portion of  $5 \pm 1.0$  gram of NTO (weighed to  $\pm 0.1$  mg) to a 150 ml beaker (w). Add 100 ml of distilled water and stir until the NTO is completely dissolved. Add precisely 5 ml of the 0.3 g/l NaCl solution with a pipette. Add 5 ml of the 30% concentrated HNO<sub>3</sub> solution. Then, using the potentiometric titrator, titrate with the 0.02 N AgNO<sub>3</sub> solution. The titrator determines the equivalence point, which is the point where the addition of a minimum amount of AgNO<sub>3</sub> titration solution leads to a maximum change in potential. A minimum of three tests shall be conducted. A minimum of three blank tests without NTO shall also be conducted.

#### Calculation and reporting

The chloride concentration is calculated as follows:

$$\%Cl = \frac{35.5 * (V_1 - V_0) * 100 * N}{1000 * w} \quad (\text{eq. 6.2.3.1})$$

w = weight of NTO (g)

V<sub>1</sub> = volume in ml of AgNO<sub>3</sub> solution used to reach the equivalence point with weight “m” of NTO. The average of a minimum of three tests is used.

V<sub>0</sub> = volume in ml of AgNO<sub>3</sub> solution used to reach the equivalence point without NTO. The average of a minimum of three tests is used.

N = normality of AgNO<sub>3</sub> solution (mole/L)

35.5 = atomic weight of chlorine (g/mole)

### Precision

With a 5 g sample, the maximum tolerated amount of ammonium chloride is 0.02% which would correspond to approximately 1mg chloride, respectively 0.03mmole, consuming 1.5 mL of silver nitrate solution. Given a volumetric resolution of 50µL, the theoretical precision is approximately 3%.

## **4.3 DETERMINATION OF SULFATE**

### **4.3.1 Determination of Sulfate (as (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>) in AN and AP**

#### Principle

Sulfates are precipitated as BaSO<sub>4</sub> after reaction with BaCl<sub>2</sub>.

#### Equipment

- 400 ml beaker
- boiling water bath
- sintered glass crucible (Grade No. 4)
- oven
- desiccator

#### Reagents

- water, analytical grade
- concentrated hydrochloric acid
- barium chloride solution

### Procedure

Dissolve  $10 \text{ g} \pm 0.1 \text{ g}$  of sample ( $W_1$ ) in distilled water in a 400 ml beaker. Add 2 ml of concentrated hydrochloric acid, and heat to boiling. Add slowly 10 ml of barium chloride solution (100 g/litre), stirring continuously during the addition. Place the beaker and contents in a boiling water bath to digest for about 30 minutes, then allow to stand overnight. Filter off any precipitate on a tared ( $W_2$ ) sintered glass crucible (Grade No. 4) and wash thoroughly with water. Dry in an oven at  $120 \pm 2^\circ\text{C}$  for one hour. Cool in a desiccator and weigh ( $W_3$ ).

### Calculation

Percentage sulfate as  $(\text{NH}_4)_2\text{SO}_4 = 100 \cdot (W_3 - W_2) \cdot 0.566 / W_1$  (eq. 4.3.1.1)

$W_2$  = weight of sintered glass crucible (g)

$W_3$  = weight of sintered glass crucible and precipitate (g)

The factor of 0.566 in the equation is the ratio of the molecular weights of ammonium sulfate (132.14 g/mole) and barium sulfate (233.39 g/mole).

### Precision

Example AN:

The maximum allowed quantity is 0.02% as  $(\text{NH}_4)_2\text{SO}_4$ . This corresponds to 3.5mg precipitation of  $\text{BaSO}_4$ . With an accuracy of 0.1mg, this amount can be measured with a precision of 3%rel.

## 4.4 DETERMINATION OF NITRITES IN AMMONIUM NITRATE

### 4.4.1 Colorimetric Method

#### Principle

Nitrites react with sulfuric acid and meta-phenylene diamine, developing a yellowish-brown colored solution. The intensity of the sample solution is compared with one standard solution of known nitrite amount, corresponding to a limited nitrate concentration specified by a purchaser. This comparison has to be carried out by using a spectrophotometer.

#### Apparatus

- volumetric flask, 100 ml
- pipette, 1 ml
- pipette, 2 ml
- analytical balance
- beaker, 50 ml
- measuring cylinder, 50 ml
- spectrophotometer

#### Reagents

- distilled water, analytical reagent grade
- aqueous sulfuric acid solution 10% by weight, analytical reagent grade
- aqueous meta-phenylene diamine solution, 0.5 % by weight, analytical reagent grade
- aqueous sodium nitrite solution, analytical reagent grade (concentration according to a specification of a purchaser; a concentration of 0.1360 g/l corresponds to 0.01 % nitrite content)

#### Procedure

Prepare a test solution consisting of 1 g of sample dissolved in 20 ml of water, 1 ml of the sulfuric acid and 1 ml of the meta-phenylene diamine solution.

Prepare a comparative solution, consisting of 19 ml of water, 1 ml of the sodium nitrite solution, 1 ml of the sulfuric acid solution and 1 ml of the meta-phenylene diamine solution. Compare the colors.

### Reporting

If the color of the first test solution is less intense than the comparative solution, the content of nitrites is less than the limit specified by a purchaser. If it is more intense, then the nitrite concentration exceeds the given limit.

## **4.5 DETERMINATION OF NITRATE IN AMMONIUM PERCHLORATE**

### **4.5.1 Colorimetric Determination as Azo-Compound**

#### Principle

Zinc metal and acetic acid are added to a solution of the sample.

Any nitrate present is reduced to nitrous acid, which is used to diazotize sulfanilic acid. The diazo-compound is then reacted with 1-naphthylamine-7-sulfonic acid (Cleve's acid) to form an azo compound, which is measured colorimetrically.

#### Reagents

- sulfanilic acid solution: Add 30 ml of glacial (17 M) acetic acid to 70 ml of water and dissolve 1 g of sulfanilic acid in the mixture, warmed as necessary.

- Cleve's acid solution: dissolve 0.5 g of Cleve's acid (1-naphthylamine-7-sulfonic acid) in 120 ml of water warming in a water bath. Filter and cool the solution. Then add 30 ml of glacial (17 M) acetic acid. Store in a brown bottle.

- standard nitrate solution: dissolve 1.00 g of ammonium nitrate in distilled water in a 100 ml graduated flask and fill up to the mark with distilled water. Transfer 1.0 ml of the solution to a 1 litre graduated flask and fill up to the mark with water. This solution must be freshly prepared.

1 ml = 0.01 mg of  $\text{NH}_4\text{NO}_3$  = 0.001 %  $\text{NH}_4\text{NO}_3$  for 1 g of sample.

- "nitrate free" ammonium perchlorate: "Laboratory reagent" grade ammonium perchlorate, available from EIDH Limited, or equivalent, has been found suitable for this purpose.

- zinc dust

- glacial acetic acid

#### Procedure

Dissolve  $1 \pm 0.1$  g of sample in 30 ml of water in a 50 ml Nessler tube. Prepare working standards by dissolving  $1 \pm 0.1$  g of "nitrate-free" ammonium perchlorate in

30 ml of water in each of five similar Nessler tubes. Add, each to a separate cylinder, 1, 2, 3, 4, and 5 ml of the standard nitrate solution, then treat these and the sample solution in the same manner.

Ensure that the temperature of the solutions is below 15°C during the remainder of the procedure. Add to each solution about 0.1 g of zinc dust and 2 ml of glacial acetic acid, and mix thoroughly. Add 2.0 ml of the sulfanilic acid solution and 2.0 ml of the Cleve's acid solution. Fill up to the mark with water, mix thoroughly, and allow the solutions to stand for 15 minutes.

Compare the intensities of the color, if any, of the sample solution with those of the standards.

#### Calculation

Percentage Nitrate as  $\text{NH}_4\text{NO}_3 = n * 0.001$  (eq. 4.5.1.1)

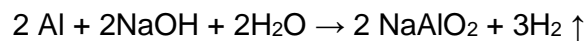
where  $n$  = volume in ml of the standard nitrate solution in the working standard solution which matches the sample solution.

## **4.6 DETERMINATION OF ACTIVE ALUMINIUM CONTENT**

### **4.6.1 Determination of Active Aluminium Content by Measurement of Evolving Gas on Treatment with Sodium Hydroxide Solution**

#### Principle

The free metallic aluminium shall be determined by measuring the volume of gas evolved when a weighed quantity of aluminium powder is reacted with sodium hydroxide solution



A method equivalent to the procedure described hereafter will be acceptable.

#### Apparatus

The basic apparatus is depicted in Annex A, Figure 2. It is advisable to house the apparatus in a separate room, free from draughts and away from direct sunlight and sources of heat.

Reagents

- 20 % M/V sodium hydroxide solution
- Chromosulfuric acid

Calibration of receiver (Letters in paragraph refer to figure 2 in annex A)

Liquids may be introduced into (R) by attaching a tube to the outlet of tap S<sub>2</sub> which dips into a vessel containing the required liquid, turning S<sub>1</sub> and S<sub>2</sub> to the appropriate positions and applying suction to the open arm of S<sub>1</sub>. Thoroughly clean the receiver (R) with chromosulfuric (chromic) acid and rinse well with water. Fill the bottle (B) about three-quarters full with water. Ensure that the open arm of S<sub>2</sub> is free from liquid by applying gentle pressure to the open arm of S<sub>1</sub> to blow out any trapped liquid. Turn S<sub>2</sub> to connect (R) with (B) and apply gentle pressure (using manometer (M) as guide) via tap S<sub>3</sub> to force water into (R) until it is filled to the mark A. Check that no air bubbles are trapped on the walls of (R). Close tap S<sub>2</sub> and release the pressure on S<sub>3</sub>. Open tap S<sub>2</sub> to the exit arm and run out the volume of water, contained in (R), into a suitable tared receiver (W<sub>1</sub> ± 10 mg) and weigh (W<sub>2</sub> ± 10 mg). Note the temperature of the water (T<sub>1</sub> °C).

$$\text{Volume of the receiver } (V_1) = \frac{W_2 - W_1}{d_1} \quad (\text{ml}) \quad (\text{eq. 4.6.1.1})$$

where d<sub>1</sub> = density of water at T<sub>1</sub>°C (g/ml)

W<sub>1</sub> = weight of tared receiver (g)

W<sub>2</sub> = weight of filled receiver (g)

Procedure (Letters in brackets refer to figure 2 in annex A)

Ensure that the bottle (B) is at least three-quarters full of water. Open tap S<sub>1</sub> to the atmosphere and adjust tap S<sub>2</sub> to connect (B) with (R). Open tap S<sub>3</sub> and apply gentle pressure (using manometer (M) as guide) via the open limb of S<sub>3</sub> to force water into (R) until it is filled to just above the mark A. Close tap S<sub>2</sub> and release the pressure on tap S<sub>3</sub>. Carefully adjust tap S<sub>2</sub> to allow the level of water in (R) to fall to coincide with the mark A. Adjust tap S<sub>1</sub> so that both (R) and (X) are connected to the atmosphere. Fill the burette with sodium hydroxide solution and adjust the level to zero and wash any excess alkali from the tip of the burette to prevent any premature reaction with the sample. Weigh accurately 0.355 to 0.365 g (W<sub>3</sub>) of the sample and transfer quantitatively to the reaction vessel (X). Add 20 cm<sup>3</sup> of water to (X) and immediately connect it firmly to the apparatus. Allow (X) and its contents to reach equilibrium and, after ensuring that the level of water in (R) is still at the mark A, adjust S<sub>1</sub> so that (R) is connected to (X) only. Close tap S<sub>3</sub> and adjust tap S<sub>2</sub> to connect (R) with (B). Record the temperature (T<sub>2</sub>) shown by thermometer (C). Check the position of all taps and run the sodium hydroxide drop wise into (X), controlling the rate of addition of alkali very carefully to prevent gas being evolved too quickly. If necessary, the reaction flask may be cooled by immersing it in a beaker of cold water. Maintain the

pressure in (R), as indicated by the manometer (M), slightly below atmospheric by opening tap S<sub>3</sub> from time to time during the evolution of hydrogen. Continue the addition of alkali until a total of 20.0 cm<sup>3</sup> has been added to (X). Swirl the contents of (X) to ensure that no unreacted sample remains. Allow the apparatus to stand for approximately 1 hour, to allow the temperature to reach equilibrium. Note the temperatures (T<sub>3</sub> °C) and (T<sub>4</sub> °C) indicated by the thermometers (C) and (D) respectively. Adjust the level of the water in the receiver (R) to that of the water in the manometer (M) by releasing or applying pressure to the open end of S<sub>3</sub>. Close tap S<sub>2</sub>. Owing to the capillary effects, the liquid levels in (R) and (M) are in equilibrium when the bottom of the meniscus in (M) is level with the top of the meniscus in (R). Turn S<sub>1</sub> to open (R) to the atmosphere and run the remaining water from (R) through S<sub>2</sub>, into a tared 250 cm<sup>3</sup> conical flask (W<sub>4</sub> ± 10 mg). Weigh the flask immediately (W<sub>5</sub> ± 10 mg). Record the atmospheric pressure (P).

### Calculation

Volume of water remaining in receiver R.

$$V_3 = \frac{W_5 - W_4}{d_2} \quad (\text{ml}) \quad (\text{eq. 4.6.1.2})$$

where d<sub>2</sub> is density of water at temperature T<sub>4</sub>°C. (g/ml)

$$\text{Free metallic Al (uncorrected) (\%)} = \frac{(P - x - y) * (V_1 - V_3 - V_2) * 0.02884}{(273.15 + T_4) * W_3} = A \quad (\text{eq. 4.6.1.3})$$

P = barometric pressure [mm Hg]

x = water vapour pressure at temperature T<sub>3</sub> [mm Hg]

y = barometric correction (for brass scale) [mm Hg]

V<sub>1</sub> = volume of receiver (R) [ml]

V<sub>2</sub> = volume of sodium hydroxide solution added [cm<sup>3</sup>]

V<sub>3</sub> = volume of water remaining in the receiver [cm<sup>3</sup>]

T<sub>4</sub> = ambient temperature of apparatus [°C]

W<sub>3</sub> = weight of sample [g]

$$0.02884 = \frac{2 * \text{atomic weight Al} * 273.15^\circ\text{C}}{3 * \text{molec. volume H}_2 * 760 \text{ mm Hg}} * \frac{100}{1000}$$

If pressure is measured in hPa, the conversion factor changes to 0.02163.

When quantities of elemental zinc and silicon are present in the sample the following correction must be made:

Free metallic aluminium (corrected) (%) = A - (% zinc content \* 0.27) - (% silicon content \* 1.28).



(eq. 4.6.1.4)

The numbers 0.27 and 1.28 derive from the ratio of the amount of hydrogen formed and the ratio of the atomic weights of the elements Al, Zn and Si.

**NOTE:** It is advisable to try to ensure that the final temperature  $T_3$  is within  $0.2^\circ\text{C}$  of the initial temperature  $T_2$  otherwise the following correction will be significant and must be taken into consideration.

#### Dead space correction

Volume of hydrogen evolved will be:

$$(V_1 - V_2 - V_3) + C \quad (\text{eq. 4.6.1.5})$$

where C is the volume correction to be applied due to the expansion or contraction of gas in the dead space. If  $T_2$  differs from  $T_3$  then:

$$C = \frac{V_4 * (T_2 - T_3)}{273.15} \quad (\text{eq. 4.6.1.6})$$

where  $V_4$  is the volume of dead space. If  $T_3$  is greater than  $T_2$  then 'C' is negative.

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ANNEX A FIGURES

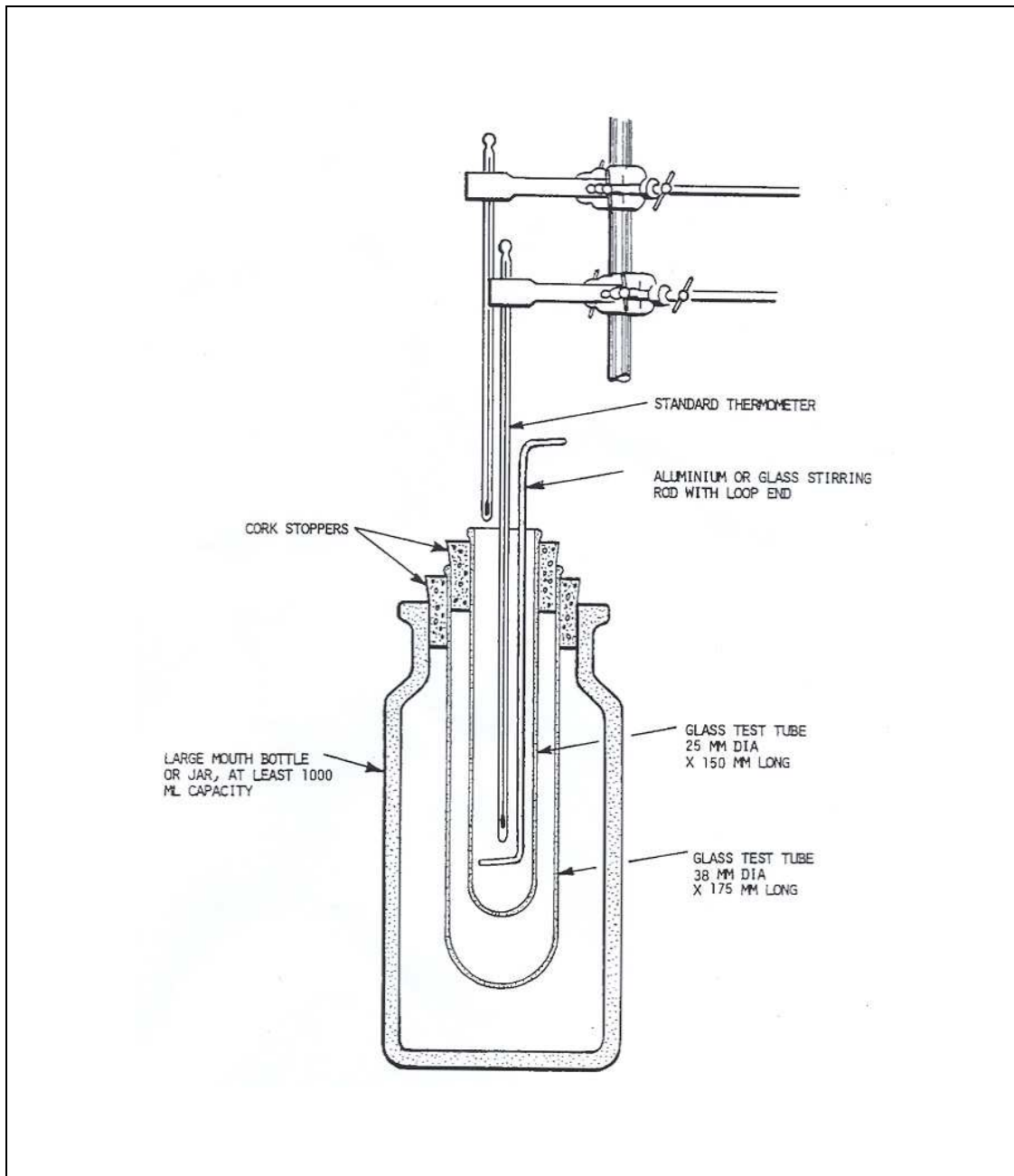


Figure 1: TNT solidification point apparatus

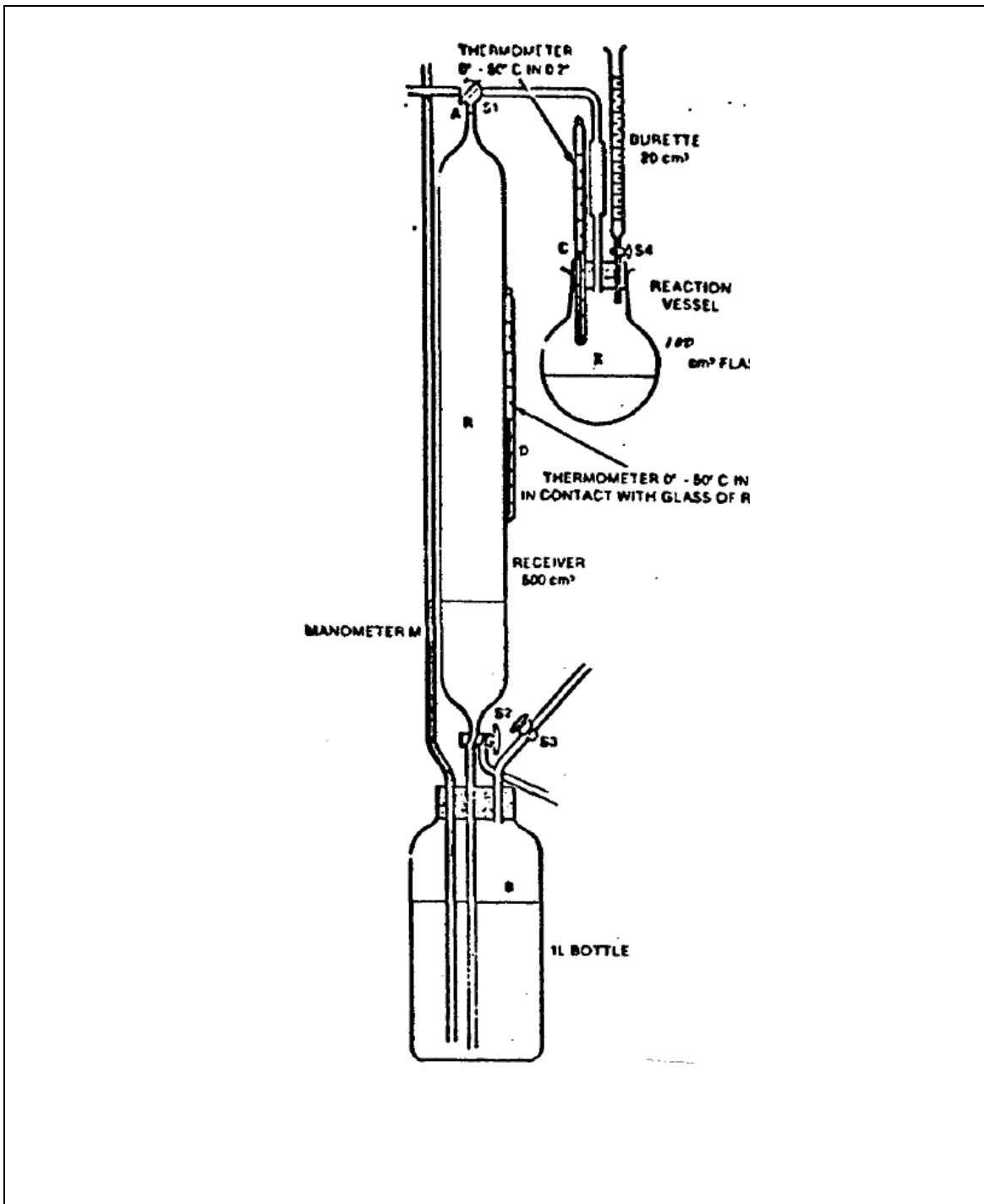


Figure 2: Apparatus for determination of active aluminium content

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**AOP-4682(A)(1)**