PS:-217/2017(3rd Rev)

PAKISTAN STANDARD SPECIFICATION
FOR
UREA FERTILIZER (PRILLED, GRANULAR, COATED AND SLOW RELEASE)

PAKISTAN STANDARDS AND QUALITY CONTROL AUTHORITY,
STANDARDS DEVELOPMENT CENTRE,
Plot No. ST-7A, Block-3, Scheme 36, Gulistan-e- Johar
Karachi.

PAKISTAN STANDARDS SPECIFICATION FOR UREA FERTILIZER (PRILLED, GRANULAR, COATED AND SLOW RELEASE) (3rdRevision)

0. FOREWORD

0.1 This Pakistan Standard was adopted by Standards Development Centre; PSQCA on 28th February,2017, after the draft finalized by the Fertilizers and Allied Product Technical Committee had been approved by the Chemical National Standards Committee.

0.2 The Pakistan Standard Specification was established in 1962, first revised in 1975 and second revised in 2009 and then 1St amendment October 26, 2011keeping in view the latest developments made in the industries; the committee felt it necessary to revise.

0.3 The Technical Committee felt that it is necessary to revise the specifications of urea "prilled and granular" widely used in Pakistanas fertilizer and consider coated and slow release Urea fertilizers being used all over the world for improved nutrient use efficiency. The requirements of Urea are given in Table – 1.

0.4 The Technical Committee included the Neem Coated Urea (NCU).Neem Oils suitable and economically viable for coating Urea fertilizer as it help reduce dust from product, act as anti-caking agent and improves storage life of Urea. Neem oil being natural source and environment friendly, provide better choice for coating urea than formaldehyde. Neem oil is also known to reduce nitrogen losses from applied fertilizers due to its nitrification inhibition properties, and its impact on slowing down urease activity in soil. The requirements of NCU are given in Table – 2.

0.5 The Technical Committee also considered inclusion of Sulphur Coated Urea (SCU) being slow release fertilizer for improved nutrient use efficiency. SCU is being produced and used in various countries worldwide.The requirements of SCU are given in Table – 3.

0.6 While preparing this standard the views of the Manufacturers, importers, testing authorities, experts, all stakeholders and consumers, were taken into consideration by the Technical Committee. Due weightage to the need or international co-ordination among standard prevailing in different countries of the world was also given.

0.7 For the purpose of deciding whether a particular requirement of this standard is complied with, the final value, observed or calculated, expressing the result of a test or analysis shall be rounded off in accordance with PS: 103 – 1991 "Rules for Rounding Off Numerical Values". The number of places retained in the rounded off value should be the same as those of the specified value in the standard.

0.8 This standard is intended chiefly to cover the technical provisions relating to the supply of the material, and it does not include all the necessary provision of a contract.

0.9 In order to keep abreast with the progress of trade and Industry Pakistan Standards are revised periodically. Suggestions from the members are welcomed and will be placed before the Technical Committees for consideration at the time of revision.

1.0 SCOPE

1.1 This Pakistan Standard describes the requirements and methods of test for prilled and granular urea, Neem coated Urea and Sulphur coated urea intended to be used as fertilizer.

2.0 DESCRIPTION-

Urea fertilizer (prilled & granular) are described below and other term used in this standard shall conform PS: 582 – 1996.

2.1 ***Prilled Urea***:-Particles of near spherical form usually of 1-3 mm particle diameter made by the solidification molten urea, that is almost anhydrous is forced through spray heads or spinner buckets at the top of a tower to produce droplets that fall through a countercurrent stream of air in which they solidify to form prills.

2.2 ***Granular Urea***:-Fertilizer characterized by spheroid particles, usually 2-4 mm in diameter 90 percent and 4 mm in diameter 7 percent, and formed by any of a number of granulation process.

2.3 ***Anticaking agent***:-Formaldehyde (CH_2O) is used as anticaking agent which is effective in dosage of only 0.2 to 0.5%. This amount of additive does not lower nitrogen content below 46%. In addition to providing anti caking of the final product, Formaldehyde (CH_2O) improves the granulation process by reducing dust formation. Maximum limit of Formaldehyde is also covered as it is considered as health hazardous chemical in urea fertilizer.

2.4 ***Neem coated urea***: - Neem oil is used as coating agent which is effective in dosage of 0.035 to 0.05% i.e. 350-500 ppm (Azadirachtin50-70 ppb). This amount of additive does not lower nitrogen content below 46%. In addition it acts as anti-caking agent for the final product and improves the granulation by reducing dust formation.

2.5 ***Sulphur coated Urea*: -** Sulphur coating of prilled or granular urea has the main objective to make it slow release. Sulphur coating is found effective when applied in the range of 10-20% and the Nitrogen content is achieved in the range of 30-40%.

3.0 **STORAGE:-**

3.1 Bags containing prilled urea should not be stored within 76 cm of building walls or partitions to allow for circulation of cooling air. Because pressure enhances caking, bagged material should not be stacked too high. Because of caking include plasticity or softness of particles, pressure in storage, temperature changes, and absorption of moisture.

3.2 However, in the absence of preventive measures, a volume change that accompanies a crystal transition at 32.3^0C causes degradation of crystals, prills, and granules, which increases susceptibility to moisture absorption and caking.

3.3 Because of caking include plasticity or softness of particles, pressure in storage, temperature changes, and absorption of moisture.

4.0 **REQUIREMENT:**

4.1 The material shall free flowing and free from harmful substances at the time of loading and shall comply with the requirement specified below for each type of Urea when tested according to the methods prescribes in column – 5 of respective Table-1

Table-I
Requirement table for urea fertilizer (Prilled and Granular)

S.#	Characteristics	Requirements		Appendix
		Prills	Granules	
(1)	(2)	(3)	(4)	(5)
1.	Physical condition	White, Free flowing Prills	White, Free flowing granular	Visual inspection
2	Moisture% by weight, max	0.5%	0.5%	B
3	Nitrogen content % by weight min.	46%	46%	C
4	Biuret% by weight max	1.5 %	1.5 %	D
5	Formaldehydes % by weight. Max]	0.7 %	0.7 %	E
6	Free Ammonia. max	250 ppm	250 ppm	F
7	Size Distribution (In diameter) 90%	1 to 3 mm 90%	+ 2 to 4 mm, 90% Min + 4 mm, 7 % Max - 2 mm, 3 % Max	G
8	Crushing strength, min	---	2 Kg	H

Table-II
Requirement table for Neem Coated Urea fertilizer (Prilled and Granular)

S.#	Characteristics	Requirements		Appendix
		Prills	Granules	
1.	Physical condition	White to Light Yellow, Free flowingPrills	White to Light Yellow, Free flowing granules	Visual inspection
2	Moisture% by weight, max	0.5%	0.5%	B
3	Nitrogen content % by weight min.	46%	46%	C
4	Biuret % by weight max	1.5 %	1.5 %	D
5	Neem oil content as Azadirachtin, min	50 ppb	50 ppb	I
6	Free Ammonia. max	250 ppb	250 ppb	F
7	Size Distribution (In diameter) 90%	1 to 3 mm 90%	+ 2 to 4 mm, 90% Min + 4 mm, 7 % Max - 2 mm, 3 % Max	G
8	Crushing strength, min	---	2 Kg	H

Table-III
Requirement table for Sulphur Coated Urea fertilizer (Prilled and Granular)

S.#	Characteristics	Requirements		Appendix
		Prills	Granules	
1.	Physical condition	Light to dark yellow, Free flowing Prills	Light to dark yellow, Free flowing granular	Visual inspection
2	Moisture% by weight; max	1.0%	1.0%	B
3	Nitrogen content % by weight; min.	32%	32%	C
4	Biuret % by weight; max	1.5 %	1.5 %	D
5	Sulphur content; min	13%	13%	J

6	Size Distribution (In diameter)	1 to 3 mm 90%	+ 2 to 6 mm, 90% Min + 6 mm, 7 % Max - 2 mm, 3 % Max	G

5.0 **SAMPLING:**

5.1 Representative sample of the material shall be drawn as prescribed in Appendix – A.

6. **PACKING AND MARKING:**

6.1 **Packing**:- The material shall be packed and supplied in sound, strong, moisture proof packages or container (natural/synthetic fiber bags are of multi wall paper with a bitumen or polyethylene moisture - proofing layer. Mono film bags of heavy (0.15-0.2 mm thickness) polyethylene also are satisfactory or in such other suitable containers) as agreed to between the purchaser and the vendor. Jute or woven polypropylene bags with mono film plastic liners shall also be used.

6.2 The weight of the material in a bag should be 25 Kg or 50 Kg net.

6.3 Marking- The container / sack shall be securely closed and marked with the following information:

(a) Name of the material

(b) Minimum nutrient content of the material

(c) Nameand Address of the manufacturer/ distributor

(d) recognized trade mark if any

(e) Net Weight in kg of the material in the container/ bag

(f) Best before Use.

(g) Any information required by law enforcement agencies or by the buyer.

APPENDIX – A

SAMPLING OF UREA, NEEM COATED UREA & SULPHUR COATED UREA FERTILIZER (PRILLED AND GRANULAR)

A-1 **GENERAL REQUIREMENTS OF SAMPLING**

A-1.0 In drawing preparing, storing and handling test samples, the following precautions and directions shall be observed.

A-1.1 Sampling shall be taken at a place protected from damp air, dust and soot.

A-1.2 The sampling instruments shall be clean and dry when used.

A-1.3 Precautions shall be taken to protect the samples, the material being sampled, the sampling instruments and the containers for samples from adventitious contamination.

A-1.4 To draw a representative sample, the contents of each container selected for sampling shall be mixed as thoroughly as possible by suitable means. Sample must be homogeneous, representative and random and applied √n+1 formula for sampling in bags.

A-1.5 The samples shall be placed in clean, dry and air, tight glass or other suitable containers on which the material has no action.

A-1.6 The sample containers shall be of such a size that they are almost completely filled by the sample.

A-1.7 Each sample container shall be sealed air tight after filling and marked with full details of sampling, the date of sampling, year of manufacture, and other important particulars of the consignment.

A-1.8 Samples shall be stored in a cool and dry place.

A-2.0 **SCALE OF SAMPLING:**

A-2.1 ***Lot:*** – All the containers in a single consignment of the material drawn from a single batch of manufacture shall constitute a lot. If a consignment is declared to consist of different batches of manufacture, the batches shall be marked separately and the groups of containers in such batch shall constitute separate lots. In the case of consignment drawn from a continuous process, 1,000 containers (or 100 metric tons of the material) shall constitute a lot.

A-2.2 The number of containers to be chosen from a lot shall depend on the size of the lot and shall be in accordance with column 1 and 2 of Table IV.

TABLE – IV

NUMBER OF CONTAINERS TO BE SELECTED FOR SAMPLING

Lot Size	No. of Containers to be selected
N	n
(1)	(2)
Upto 4	All
Up to 100	5
101 to 300	6
301 to 500	7
501 to 800	8
801 to 1300	9
1301 and above	10

A-2.3 These containers shall be chosen at random from the lot, and in order to ensure randomness of selection the following procedure may be adopted.

A-2.3.1 Arrange all the containers in the lot in a systematic manner and starting from any container, count them 1,2,3, …… etc up to r and so on, r being equal to the integral part of N/n. Every rth containers thus counted shall be withdrawn and all such containers shall constitute the sample.

A-3 **TEST SAMPLE AND REFREE SAMPLE:**

A-3.1 Draw with an appropriate sampling instrument small portions of the material from different parts of the containers selected, the total quantity taken out from each container being sufficient to conduct the tests for all characteristic given in 2.

A-3.2 Mix thoroughly all portions of the material drawn from the same container to form an individual test sample. Equal quantities from all individual test samples so formed shall be mixed together to form a composite test sample.

A-3.3 All the individual test samples and the composite test sample shall be divided into three equal parts, thus forming three sets of test samples. These parts shall be immediately transferred to thoroughly dried bottles which shall then be sealed air tight with glass stopper. One of these sets of test sample shall be sent to the purchaser and another to the vendor.

A-3.4 ***Referee Sample*** – The third set of test samples bearing the seals of the purchaser and the vendor, shall constitute the referee sample and shall be used in case of dispute between the purchaser and the vendor. It shall be kept at a place agreed to between the purchaser and the vendor.

A-4 **NUMBER OF TEST:**

A-4.1 Test for the determination of total nitrogen shall be conducted on each of the individual test samples.

A-4.2 Test for the remaining characteristics given in 3 shall be conducted on the composite tests sample.

A-5. **CRITERION FOR CONFORMITY:**

A-5.1 The test results for total nitrogen shall be recorded as shown in Table ~~III~~V. The mean and the range of the test result shall be calculated as follows:

Mean (X) = $\frac{\text{The sum of the test results}}{\text{Number of test results}}$

Range (R) = the difference between the maximum and the minimum values of the test results.

A-5.1.1 The appropriate expression as shown in col.6 of Table-V~~III~~ shall be calculated for this characteristic. If the condition given in col.6 of Table-V~~III~~ is satisfied, the lot shall be declared to have satisfied the requirement for this characteristic.

A-5.2 For the remaining characteristics, the test results on the composite test sample shall satisfy the requirements specified in 3.

A-5.3 A lot shall be declared as conforming to the specification only when it has satisfied each of the requirements specified in 3.

TABLE – V~~III~~

CRITERION FOR CONFORMITY

S.#	Characteristic	Test Results 1.2 n	Mean	Range	Criterion for Conformity
I	ii	iii	iv	v	vi
1	Total nitrogen, percent by weight	--	$\bar{X}$	R	$\bar{x}$–0.6 R≥ the value specified in Table (1) 3

APPENDIX B

B-A- **DETERMINATION OF MOISTURE IN UREA(KARL-FISHER METHOD)**

B-A-1 **Apparatus:**

B-A-1.1 ***Potentiometer titrator***-equipped with magnetic stirrer and auto control.

B-A-2 **Chemicals:**

B-A.2.1 Karl-Fisher Reagent.

B-A.2.2 Standard water-methanol solution.

B-A.2.3 Methanol Purified or Karl Fisher solvent

B-A.3 **Procedure:**

B-A.3.1 ***Estimation of factor*** - Place 30 ml. of purified methanol or Karl Fisher solvent in the titration flask of the titrate and titrate to the end point with Karl-Fisher reagent. For end point follow the instruction of the manufacturer of the apparatus. Add 0.2 to 0.3 g of sodium tartrate dehydrate and titrate with Karl-Fisher reagent to the end point. Sodium tartrate dehydrate contains 15.65% water.

$$F = \frac{H}{a}$$

Where,

F = Factor of the reagent (mg/ml).
a = ml. of Kari-Fisher reagent required for sodium tartrate dihydrate.
H = mg. of water contained in sodium titrate dihydrate taken.

$$= \frac{15.65 \times 1000}{100} \times \text{wt. of tartrate taken}$$

B-A.3.2 ***Determination*** - Place 30 ml. of purified methanol or Karl Fisher solvent in the titration flask of the titrator and titrate with Karl-Fisher reagent to the end point. Add 1-- 2 gram of the sample, dissolves thoroughly, and titrates with Karl-Fisher reagent to the end point.

B-A.3.3 ***Calculations:***

$$H_2O\% = \frac{Y \times F}{S \times 10}$$

Where,

Y = ml. of Karl-Fisher reagent consumed for the sample.
S = gram of the sample taken.

APPENDIX – C.

C- DETERMINATION OF TOTAL NITROGEN IN UREA

C-1.0 ***Apparatus.*** – Distillation apparatus for determining total nitrogen and Ammonical Nitrogen. Distillation apparatus shall consist of Alkali-resistant, glass Rubber stoppers must be renewed periodically and should fit closely in the neck of the distillation flask, to prevent condensation of liquid between glass walls and the stopper or Automatic Kjeldahl Distillation Unit.

C-2.0 **Reagent:**

C-2.1 *Potassium Sulphate:* - anhydrous (sodium sulphate may be used if potassium sulphate is not available).

C-2.2 *Copper Sulphate.*

C-2.3 *Concentrated Sulphuric Acid.*

C-2.4 *Standard Sulphuric Acid* – 0.5 N.

C-2.5 *Mixed Indicator* – Mix 1:1 ratio (v/v) 0.2% solution of methyl red 0.1 percent solution methylene blue both in alcohol.

C-2.6 *Sodium Hydroxide Solution* – Approximately 40 percent (w/v).

C-2.7 *Standard Sodium Hydroxide Solution* – 0.5 N.

C-3.0 ***Procedure*** –

C-3.1 Weigh accurately about 0.5 g of the prepared sample and transfer to a Kjeldahl flask. Add 10 g of powdered potassium sulphate and a few crystals of copper sulphate. Add 30 ml of concentrated Sulphuric acid to the flask. Place the flask in an inclined position. Heat below the boiling point until forthing ceases. Raise the temperature to bring the acid to brisk boiling. Continue the heating until the solution becomes straw-yellow in colour for practically water-white. Now remove the flask from the flame and cool. Transfer quantitatively to the round bottom flask and dilute to about 250 ml with water.

C-3.2 Add about 60 ml or more, if necessary, to make the solution alkaline of sodium hydroxide solution carefully down the side of the flask so that it does not mix at one with the acid solution but forms a layer below it. Assemble the apparatus with the tip of the condenser dipping in a known quantity of standard Sulphuric acid in excess that required to neutralize the ammonia to be evolved beaker to which a few drops of mixed indicator have been added. Mix the contents of the flask by shaking and distill until all ammonia has passed over. Detach flaskfrom the condenser and shut off the burner. Rinse the condenser thoroughly with water into the beaker. Wash, the dip tube carefully so that all traces of the condenser are transferred to the beaker. When all the washings have drained into the beaker, add two a three drops more of the indicator and titrate with standard sodium hydroxide solution.

C-3.3 Carry out a blank using all reagents in the same quantities without the material to be tested.

C-3.4 Calculation:

Total nitrogen, percent by weight = $\frac{1{,}400\ (B - A)\ N}{W}$

Where,

B = volume in ml of standard sodium hydroxide solution used to neutralize the acid in blank determination.

A = volume in ml of standard sodium hydroxide solution used to neutralize the excess of acid in the test with the material.

N = normally of standard sodium hydroxide solution, and

W = weight in g of the prepared sample taken for the test.

APPENDIX – D.

D **DETERMINATION OF BIURET CONTENT OF UREA (COLORIMETRIC METHOD)**

D-1.0 **Summary of Method:**

A known weight of sample is stirred in a CO_2-free distilled water to dissolve the biuret and the solution is filtered. The filtrate is passed through an ion exchange column to remove interferences such as ammonium ions. The eluate is then treated with copper sulphate in the presence of alkaline tartrate solution; the biuret in the sample reacts to form a copper complex, the intensity of which is proportional to the biuret content. The colour intensity is measured at 550 m µ and with the absorbance known, the percent biuret is determined from the calibration curve. Results are reported to the nearest 0.01 weight percent.

D-2.0 **Apparatus**

D-2.1 ***Spectrophotometer***- Capable of measuring absorbance at 555 nm, and wash the Beckman DU instrument, Photoelectric colorimeters fitted with a 500 – 570 nm (or 520 580nm) filter are acceptable.

D-2.2 ***Absorption Cell*** - Matched Pair 50 mm, light path length;

D-2.3 ***Water Baths*** - Capable of maintaining temperature of 30 ± 5^0C and 50 ± 5^0C.

D-2.4 ***Filter Paper*** - Whatman 1 or its equivalent,

D-3.0 **Reagent:**

D-3.1 Unless otherwise indicated, the purity of the following materials should be of reagent grade.

D-3.2 CO_2 Free Distilled Water: (pH 6.5 at 25^0C). Prepare by boiling distilled water. Cool, prepare fresh daily.

D-3.3 *Alkaline Tartrate Solution* – Dissolve 40 g of sodium hydroxide in 500 ml of water, stopper the container and allow to cool. Add 50 g, of sodium potassium tartrate ($NaKC_4H_4O_6$ $4H_2O$), and agitate the solution to dissolve the crystals,. Dilute to 1 litre and mix well. Allow the solution to stand one day before use.

D-3.4 *Copper Sulphate Solution*: - Dissolve 15 g. of copper sulphate ($CuSO_4$. $5H_2O$), in CO_2-free distilled water and dilute to 1 litre.

D-3.5 *Biuret Standard Solution* – 1 mg/ ml. Dissolve 250 ± 1 mg. of biuret in CO_2-free distilled water and dilute to the mark in a 250 ml. volumetric flask.

D-3.6 *Methyl Red Indicator* - Dissolve 1 g. of methyl 1 red in 200 ml. of ethyl alcohol.

D-3.7 *Sulphuric Acid- **0.1N*** – Add 2.3ml of concentrated sulfuric acid to approximately 500 ml. of water in a 1-litre volumetric flask and fill to the mark with additional water. Mix well. Standardization of the solution is not required.

D-3.8 *Ion Exchange Resin* – Fill a 50 ml. biuret with 30 cm. column of Amberlite IR 120 (H) resin on a glass wool plug. (Regenerate the column after each use by passing 100 ml. of H_2SO_4 (1:9) or HC1 (1:4) through the column at 5 ml./min., then wash with water until the pH of the effluent is greater than (6). The Amberlite IR 120 (H) resin is available from Rohm and Hass,Philadellphia, Pennysylvania, or a comparable ion exchange resin may be used.

D-4 **CALIBRATION:**

D-4.1 Pipette be separately 2, 10, 20, 30, 40 and 50 ml. of the biuret standard solution in 100 ml. volumetric flasks. These will contain 2, 10, 20, 30, 40 and 50 mg biuret, respectively.

D-4.2 Adjust the volume in each flask to about 50 ml. with CO_2 free distilled water.

D-4.3 Add one drop of methyl red into each flask and neutralize with 1 or 2 drops of 0.1N Sulphuric acid to a pink colour, swirl.

D-4.4 While swirling, pipette into each flask 20 ml. of alkaline tartrate solution, followed by 20 ml of copper sulphate solution.

D-4.5 Fill each flask to the mark with CO_2free distilled water and shake for 10 seconds.

D-4.6 Allow the flasks to stand for 15 minutes at 30 ± 5^0C. If the room temperature is not 30 ± 5^0C, place the flasks in a water bath maintained at 30± 5^0C.

D-4.7 Prepare a reagent blank, using the same quantities of reagents and conditions but excluding the biuret standard solution.

D-4.8 Fill one of the absorption cells with the reagent blank and place it in the light path in the spectrophotometer. Set the wave-length at 555 nm. Adjust the absorbance to zero in accordance with the instructions for the particular instrument.

D-4.9 Fill the sample cell with one of the calibration standards and determine the absorbance at 555 nms. Records the absorbance reading.

D-4.10 Repeat the absorbance measurement for each of the remaining calibration standards. All measurements should be conducted so that no standard is allowed to stand for more the 30 minutes measured from the time it was placed in the 30^0C bath.

D-4.11 Prepare a calibration curve on rectilinear paper by plotting the absorbance values against the corresponding weights of biuret in the standards in mg.

D-5.0 **PROCEDURE:**

D-5.1 Weight 10 ± 0.1g of the sample under test into a 150 ml. beaker. Dissolve in 50 ml. of the CO_2-free distilled water preheated at 50 ± 5^0C.

D-5.2 Stir the solution for 30 minutes and maintain the temperature at 50 ± 5^0C by using a water bath capable of maintaining a temperature of 50 ± 5^0C.

D-5.3 Filter the solution into a 100 ml. volumetric flask using a medium sized filter paper. Rinse the beaker and the stirrer with small portions of CO_2-free distilled water and add the rinsings to the filter. Fill the flask to the mark with CO_2-free distilled water.

D-5.4 Transfer 25 ml. aliquot of the filtrate into the ion exchange column: adjust the flow to 4-5 ml./ minute, collect the eluate in a 100 ml, volumetric flask.

D-5.6 When the liquid level reaches the top of the resin bed wash with two ml. portion of CO_2-free distilled water, and adds the washings to the eluate in the flask.

D-5.7 Add 1 or 2 drops of methyl red indicator and IN NaOH to a yellow color. Add a few drops of 0.1 N H_2SO_4 until the solution just turns pink. Fill the flask to the mark with CO_2-free distilled water, shake, and mix thoroughly;

D-5.8 Pipette 50 ml. of the solution into a 100 ml. volumetric flask and proceed as in CALIBRATION, steps (3) through (8).

D-5.9 Fill the sample cell with the sample under test and determine the absorbance at 555 mμ.

D-5.10 From the calibration curve, determine the mg of biuret that corresponds with the absorbance reading.

D-5.11 Calculation:-

(1) Calculate the percent of biuret in the sample by the following equation:

$$B = \frac{W_1 \times 100}{W \times 1000 \frac{25}{100} \times \frac{50}{100}}$$

Simplifying $$B = \frac{W1}{W \times 1.25}$$

Where,

W = is the weight of sample in g.
W1= is the biuret content of the sample as read from the calibration curve in mg.
B = is the wt. percent biuret in the sample.

$\frac{25}{100}$ $\frac{50}{100}$

The constants and are Aliquot portions.

D-5.12 Reporting:

Report the result to the nearest 0.01% as:
Biuret Content__%.

Alternate Method

Determination of Biuret content of urea (without Ion exchange column)

D-6.0 **APPARATUS / EQUIPMENT:**

D-6.1 *Spectrophotometer* with 10 mm Glass curvettecell.

D-6.1.2 *Spectrophotometer with 10 mm Glass cuvette ceil*
D-6.1.3 *Pipette*20 ml
D-6.1.4 *Volumetric flask* 100 ml, 250 ml, 1L
D-6.1.5 *Burette* 50 ml
D-6.1.6 Beaker 1L
D-6.1.7 Weighing Balance

D-6.2 **Chemicals/Reagents**

D-6.2.1 Segnette Salt Solution
Dissolve 20g sodium potassium tartarate in 600ml water. Add 32g of NaOH and dissolve completely Cool, make upto 1000ml with demin or distil water and mix thoroughly.

D-6.2.2 **Copper Sulphate Solution (6g / Litre)**

Dissolve 6.0g copper Sulphate ($CuSO_4$, $5H_2O$) in one litre of demin or distil water

D-6.2.3 **Biluret Standard Solution (1000 ppm)**

Weigh exact 1.00 g purified biuret and transfer into 1L beaker containing about 800 ml demin or distil water Dissolve at 70 °C cool and transfer solution with 2-3 washings into 1L volumetric flask. Dilute to mark and mix.

"1 ml = 1 mg biuret"

D-6.2.4 Methanol (pure)

D-6.3 Preparation of Calibration Curve (0-50 mg)

D-6.3.1 Transfer 10, 20, 30, 40 & 50 ml of Biuret stock solution in 100 ml volumetric flasks & make volume about 50 ml with demin or distil water in each flask. Each flask will contain 10, 20, 30, 40 & 50 mg biuret respectively.

D-6.3.2 Add 20ml seignette salt solution & mix.

D-6.3.3 Add 20 ml copper Sulphate solution & mix

D-6.3.4 Make the volume upto mark with demin or distil water & mix thoroughly

D-6.3.5 Make a blank with demin water and all reagents.

D-6.3.6 Wait for 15 minutes.

D-6.3.7 Note the absorbence at 550nm with 10 mm cuvette cell against blank

D-6.3.8 Draw the calibration curve between Abs,& mg of biuret & calculate factor

D-6.4.0 **METHOD**

D-6.4.1 Weigh 40g of urea sample and dissolve in water contained in 250 ml volumetric flask. Make volume upto mark with demin or distil water. Mix thoroughly.

D-6.4.2 Take 20 ml of sample in100 ml volumetric flask and make about 50 ml with demin or distil water

D-6.4.3 Proceed thru steps 2.5.2 – 2.5.7

D-6.5 CALCULATION

$$\text{Biuret \%} = \frac{\text{Factor x absorbance x 250 x 100}}{\text{wt of urea x 20 x 1000}}$$

OR

$$\text{Biuret \%} = \frac{\text{Factor x absorbance x 1.25}}{\text{wt of urea}}$$

D-6.6 REMOVAL OF INTERFERANCE OF FREE AMMONIA

D-6.6.1 Free Ammonia can interfere with determination of biuret. If concentration of Free Ammonia is less than 10 ppm its interference is negligible. If it is more than 10 ppm the proceed as below:

D-6.6.2 Take 40g sample in 1L beaker. Add 100 ml demin or distil water and dissolve urea granules completely.

D-6.6.3 Add 50 ml methanol. Mix thoroughly.

D-6.6.4 Evaporate on steam bath till about 20-30 ml volume is left.

D-6.6.5 Transfer into 250 ml volumetric flask. Wash beker thoroughly into volumetric flask. Make uupto the mark with demin or distill water and mix well.

D-6.6.6 Proceed as per step 3.2

APPENDIX – E.

E- DETERMINATION OF FORMALDEHYDEIN UREA

E-1.0 APPARATUS / EQUIPMENT:

E-1.1	*Spectrophotometer* with 10 mm cell.	
E-1.2	*Cylinder*	50 ml
E-1.2	*Volumetric Flask*s	100m l. 500ml 1L
E-1.3	*Bulb pipette*	20 ml
E-1.4	*Burette*	25 ml

E-2.0 CHEMICALS / REAGENTS

E-2.1 *Chromotropic Acid Solution* (2%)

E-2.1.1 Dissolve 2g of solid Chromotropic Acid Disodium salt in demineralized or distill water and dilute to 100ml. Filter the solution if required.

E-2.2 *Sulphuric Acid Conc.* (98%)

E-2.3 *Urea* Formaldehyde Solution (UF-85) with 60% Formaldehyde.Or Formaldehyde (37%) Solution

E-2.4 Formaldehyde Stock Solution (10ppm)

E-2.4.1 Weigh about 50 g UF-85 solution or Formaldehyde 37% solution in 1L volumetric flask containing some demineralized or distill water. Make the volume upto mark & mix thoroughly.

E-2.4.2 Measure 20 ml from above with bulb pipette & transfer into 1L volumetric flask. Dilute upto the marks & mix.

E-2.4.3 According to formaldehyde contents calculates &transfer the mls of solution from clauseE-2.4.2 in 1L volumetric flask to make formaldehyde solution of 10 ppm. Dilute up to the mark with demineralized or distilled water and mix (1ml = 10µg formaldehyde)

E-3.0 PREPARATION OF CALIBRATION CURVE (0-100 µg):

E-3.1 Transfer 2,4 6, 8 & 10 ml formaldehyde stock solution ((10ppm) in a series of 100 ml of volumetric flasks. Equivalent to 20,40, 60,80 & 100µg formaldehyde contents in each flask.

E-3.2 Add demineralized or distilled water in each flask to make total volume 10 ml in each flask.

E-3.3 Add to each flask 2ml Chromotropic acid solution and then 25 ml of concentrated H_2SO_4.

E-3.4 Allow reacting for 30 minutes without cooling.

E-3.5 Dilute the contents of the flask nearly to the mark with sulphuric acid 5 N .

E-3.6 Cool the flasks to room temperature.Fill up to the mark with sulphuric acid 5N &mix.

E-3.7 Also make a blank with demineralized water & precede thorough Clause E- 3.3 - E3-6.

E-3.8 Measure the absorbance at 570nm against blank with 10mm cell.

E-3.9 Plots graph between Abs and µg formaldehyde & calculate slope.

E-4.0 **METHOD:**

E-4.1 Weigh about 2g of urea granules and dissolve in 1L volumetric flask containing demineralized or distil water mix to dissolve and make volume up to mark.

E-4.2 Take 5 ml of above solution in 100ml volumetric flask containing 5ml demineralized water.

E-4.3 Proceed thought Clause E-3.3 to E-3.8

E-5.0 **CALCULATIONS:**

$$\text{Formaldehyde \%} = \frac{\text{Abs x Slope x 1000 x 100}}{\text{Wt of Urea x 5 x 1000 x 1000}}$$

APPENDIX– F

DETERMINATION OF FREE AMMONIA IN UREA GRANULES

F.1 **APPARATUS / REAGENTS**

F.1.1 Conical flask: 500 ml.
F.1.2 Volumetric flask: 1L.
F.1.3 Electric balance

F.2 **CHEMICALS / REAGENTS**:

F.2.1 HCl (0.1)
F.2.1.1 Dissolved about 9.0 ml of concentrated HCl (37%) in water and make the volume upto liter in volumetric flask.
F.2.1.2 Phenolphthalein (0.5) Indicator:
F.2.1.3 Dissolved 0.5 g of solid in 100 ml of methanol or ethanol.

F.3 **PROCEDURE / METHOD:**

F.3.1 Weigh about 20 g of urea granules in 500 ml conical flask.
F.3.1.1 Add about 250 ml cold demineralized water & stir to dissolve completely.
F.3.1.2 Add few drops of phenolphthalein indicator.
F.3.1.3 If pink colour appears titrate with 0.1 N HCL till disappearance of pink colour.
F.3.1.4 Note milli liter of acid used.

F.4 **CALCULATION**

$$\text{Free } NH_3 = \frac{\text{Volume of HCL used X 0.1 X 17.03 X 1000}}{\text{Wet of sample}}$$

APPENDIX – G

DETERMINATION OF SIZE DISTRIBUTION OF UREA

G.1 **APPARATUS / EQUIPMENT.**

G.1.1 *Stainless steel sieves* of the required mesh size with lid & bottom pan.

G.1.2 *Sieves Shaker*

G. 1.3 *Top Loading balance*

G.1.4 *Brush*

G-2 **METHOD:**

G-2.1 Arrange the individually tare sieves in descending order of mesh size from top to bottom.

G-2.2 Place receiving pan on the bottom of stack

G-2.3 Weigh about 200 to 300g of sample taken through sample divider.

G-2.4 Transfer sample onto the top sieve place lid on top of stack.

G-2.5 Place the sieve stack on shaker and tighten the belts evenly on both sides.

G-2.6 Set timer of vibrator to 5 minutes amplitude at 3.0 mm and start the vibrator.

G-2.7 After shaking stops switch-off the vibrator and remove the sieves one by one.

G-2.8 Weigh sieve + sample on top loading balance.

G-2.9 Calculate the weight of samples retained on each sieve.

G-3 **CALCULATION**

G-3.1 Calculate weigh percent on each sieve by following formula

$$\text{Wt. \% on each sieve} = \frac{\text{Weight (g) on sieve} \times 100}{\text{Total Weight of Sample}}$$

APPENDIX – H

DETERMINATION OF CRUSHING STRENGTH OF UREA GRANULES

H-1. **APPARATUS / EQUIPMENT:**

H.1.1 *Crushing strength apparatus*
It consists of two parts A 10 mm diameter flat-ended steel rod with plate glass on one side and a supporting scale to provide a smooth bearing surface.

H-1.2 *Plastic bottle* 5L (graduated with marker at 200 ml interval)

H-1.3 *Rubber tube*

H-1.4 Whatman filter paper No. 41

H-2. **CHEMICALS / REAGENTS:**

H-2.1 *Tap water*.

H-3 METHOD:

H-3.1 Weigh the rod of crushing strength apparatus and 5L empty plastic bottle Let their total weight as W1" Kg.

H-3.2 Collect at least 10 granules from 3 15 mm sieve size.

H-3.3 Place a granule under the rod.

H-3.4 Place the plastic bottle at the top of rod.

H-3.5 Start adding tap water slowly through rubber tube into the plastic bottle.

H-3.6 Closely observe the granules as the bottle is being filled

H-3.7 When granule breaks immediately disconnect the tap water.

H-3.8 Note down the liters of water filled in bottle Take the liters of water as W2 Kg

H-4 CALCULATION:

Crushing strength (Kg) = W1± W2

The average crushing strength for 10 granules is taken as the crushing strength in Kg for the product.

APPENDIX - I

DETERMINATION OF AZADIRACHTIN IN NEEM COATED UREA

I SUMMARY/PRINCIPLE

I-1 This method is spectrophotometric in which Azadirachtin is measured in neem oil coated Urea at 220nm in 1cm cell using uncoated Urea as blank

I-2 EQUIPMENT/APPARATUS

I-2.1 UV-Visible spectrophotometer

I-2.2 1 cm matched quartz cells

I-2.3 Volumtertic flasks of 100 and 250mL

I-2.4 Glass beakers 100 Ml

I-2.5 5cc syringe for standard preparation

I-2.6 Whatman filter paper No. 41

I-3 CHEMICALS

I-3.1 Di-Chloromethane

I-4 PROCEDURE

Standard preparation:

I-4.1 Accurately weigh about 0.035g (± 2%) pure neem oil standard in 100mL Vol. flask with the help of sringe.

I-4.2 Add 50 mL di-chloromethance and shake the flask for 30 minutes on shaker.

I-4.3 Make up the volume up to 100 mL mark with di-chloromethane and mix well.

Sample and blank preparation:

I-4.4 Accurately weigh about 100g (± 2%) neem oil coated urea sample in 250mL Vol. flask. Mark this flask as sample.

I-4.5 Accurately weigh about 100g (± 2%) uncoated urea sample in another 250mL Vol. flask. Mark this as blank.

I-4.6 Fill both flask flask half with di-chloromethane and shake for 2hrs on shaker.

I-4.7 After shaking make up the volume with di-chloromethane and mix well.

I-4.8 Filter the standard, sample and blank seperately in separate beakers with whattmann 41 filter paper.

I-4.9 Set wave length of UV-visible spectrophotometer at 220nm. Set zero by taking di-chloromethane as blank in 1cm quartz cell for standard. Fill the cell with standard and press reading. Note the absorbance as Standard Absorbance

I-4.10 Take filtered blank prepared solution of uncoated urea in 1 cm cell and set zero.

I-4.11 Fill 1cm cell with filtered coated urea sample solution and press reading. Note this reading as sample reading

I-5 CALCULATION

I-5.1 Neem oil in mg/g = $\frac{\text{Sample absorbance x weight of standard in mg x 250}}{\text{Standard absorbance x 100 x weight of sample in g}}$

I-5.2 Or Neem oil in ppm = $\frac{\text{mg/g neem oil x } 10^6}{1000}$

I-5.3 Or Neem oil as Azadirachtin ppb = ppb neem oil x 0.1429

APPENDIX - J

DETERMINATION OF TOTAL SULPHUR (S) IN SULPHUR COATED UREA

J-1 **Total Sulphur (Sulphate and Elemental) in dry fertilizers:**

J-1.1 Accurately weigh test portion containing 100-150 mg S into 400 mL beaker, add 200 mL H2O, 15 mL HCl, heat to bp, and boil gently ca 10 min. Filter through Gooch crucible containing glass fiber paper and wash with hot water. Set washed crucible aside.

J-1.2 Quantitatively transfer filtrate back to beaker and bring nearly to bp. Add slowly, with constant stirring, slight excess (ca 15 mL) 10% BaCl2 solution. Digest on low temperature hot plate adjusted so that solution does not boil, or on steam both I hr, and let stand at room temperature over night. Filter through Gooch crucible containing glass fiber paper previously dried at 250°C, cooled, and weighed. Wash with 10 portions hot water, dry crucible and contents 1 h at 250°C, cool to room temperature and weigh.

J-1.3 Percent Sulfate S = g BaSO4 x 0.1374 x 100/g test portion

J-2 **Total Sulfur in sulfur-coated urea and elemental sulfur formulations:**

J-2.1 Accurately weigh test portion containing200-300 mg S into 125 mL glass-stoppered Erlenmeyer, add ca 50 mL H2O, stopper, and shake vigorously 30 s. Filter quantitatively with suction through Gooch crucible containing glass fiber paper and wash with H2O. Proceed as in (a), beginning "Wash insoluble residue with five 10 mL portions acetone saturated with S. Dry 1 h at 100°C, cool, and weigh. Wash residue with three 5 ml portions CS2, drain, dry 1 h at 100°C, cool in desiccator, and weigh. Difference in weight = elemental S (S°).

J-3 Percent S° = g S x 100/g test portion

J-4 Percent total S = percent sulfate S + percent S°

-=-=-=-=-=-=-=-X-=-=-=-=-=-=-=-=-=-=-=-X-=-=-=-=-=-=-=-=-=-=-=-=-X-=-=-=-=-=-=-

References:

In the preparation of this standard references was made to the following:

- *Pakistan Standard PS: 582- 1996, Glossary of terms used in Fertilizer Industry (1st Revision)*
- *Encyclopedia of Chemical Technology, 4th edition, Vol: 10, John Wiley & Sons Inc. (pg: 449-451)*
- *Studies on extraction and HPLC Analysis of Azadirachtin from Kernels of Neem Seeds. Journal of Advance Pharmacy Education and Research USA. Jan-Mar 2013 Vol. 3, Issue 1.*
- *Method of Analysis: AOAC 980.02, Sulphur in Fertilizers, Gravimetric Method, First Action 1980, Final Action 1985.*