INTERNATIONAL STANDARD

ISO 23381

First edition
2020-09

Determination of salt out (crystallization) temperature of liquid fertilizers

Détermination de la température de désolubilisation (cristallisation) des engrais liquides

Reference number
ISO 23381:2020(E)

ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Email: copyright@iso.org
Website: www.iso.org

Published in Switzerland

Contents

Page

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 134, *Fertilizers, soil conditioners and beneficial substances*.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

The global liquid fertilizers market size is estimated to account for a value of USD 2,5 billion in 2019 and is projected to grow at a CAGR of 3,7 % from 2019, to reach a value of USD 3,1 billion by 2025. North America is the leading consumer of the liquid fertilizers with 32 % of the market, followed by Europe (25 %), Asia Pacific (21 %), Latin America (13 %), and the rest of the world at 9 %[7]. Liquid fertilizers cover inorganic nitrogen, phosphorus, potash, and micronutrients as well as organic, and synthetic fertilizers applied to soil, as foliar, in fertigation, and as starter solutions and aerial applications and in crops such as cereals, grains, fruits, vegetable, oilseeds, pulses, turf, ornamentals, forage, and plantation crops. Liquid fertilizers are the most efficient way of delivering the required nutrients to the plants at the correct time and in optimal concentration.

Urea ammonium nitrate (UAN 28-32) is an example of a widely used liquid fertilizer. Ammonium polyphosphate (APP, 10-34-0, and 11-37-0), Ammonium thiosulfate (ATS, 12-0-0-26S), potassium thiosulfate (KTS, 0-0-25-17S), magnesium thiosulfate (0-0-0-10S-4Mg), calcium ammonium nitrate (CAN 17), and solutions of water soluble fertilizers such as potassium nitrate (13-0-46), and ammonium chloride solution (6-0-0-16Cl) are few examples of liquid fertilizers.

Limitations of liquid fertilizers

Liquid fertilizers, although easier to use, and are versatile in application, they have the disadvantage of salting out (crystalize) at cold climate. This phenomenon creates limitation for transportation, storage, and handling during the cold season and proper steps is recommended to avoid crystallization.

Accurate crystallization data and an accurate, easy to use, and a universal method for the determination of salt out temperature (SOT) of liquid fertilizers is a helpful reference for stakeholders to avoid or prevent crystallization of these popular fertilizers during the cold season[8].

Currently, there is no uniform and standard method for the determination of SOTs of liquid (fluid) fertilizers. There are quite a few methods used internally by several manufacturing companies. ASTM D6660 for the freezing point determination of aqueous ethylene glycol base engine coolants by atomic phase transition method, ASTM D1177-17 for the determination of freezing point of aqueous engine coolants, and the ASTM D97 (pour point) have also been cited in the literature for SOT measurements of liquid (fluid) fertilizers. Pour point of a liquid is defined as the temperature below which the liquid loses its flow characteristic. [4]to[6]

In addition to these cited methods, there are ISO documents that provide methods to determine the melting/freezing temperature of chemicals. ISO 1392 provides a method for the determination of the crystallization point of chemicals, and ISO 3016 provides a method for petroleum oils for the determination of pour points. [1],[2]

Differential scanning calorimetry is a thermoanalytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference is measured as a function of temperature. Both the sample and reference are maintained at nearly the same temperature throughout the experiment. The temperature increase as a function of time linearly and heat flow curve vs. the temperature increase is the instrument output. These instruments are expensive and the price tag is over $50,000 (USD).

Moreover, OECD Guidelines refers to the term “melting range” for the transition of solid to liquid.

The proposed method is based on cooling/thawing of the liquid fertilizer. The liquid (fluid) fertilizer is cooled in a dry ice/methanol bath until the liquid is crystallized. It then warms at the ambient temperature. Normally, the SOT is the temperature at which the last crystal dissolves.

Determination of salt out (crystallization) temperature of liquid fertilizers

1 Scope

This document specifies the test procedure for the determination of the salt out temperature (SOT), also known as the crystallization temperature (CT) of liquid (fluid) fertilizers, using an inexpensive and simple technique.

This method might not be applicable to the binary and ternary fertilizers, especially with regards to the last crystal to disappear (LCTD). Some of these exceptions are discussed in the procedure (Clause 8).

2 Normative references

The following referenced documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 3696:1987, *Water for analytical laboratory use — Specification and test methods*

3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— IEC Electropedia: available at http://www.electropedia.org/

— ISO Online browsing platform: available at https://www.iso.org/obp

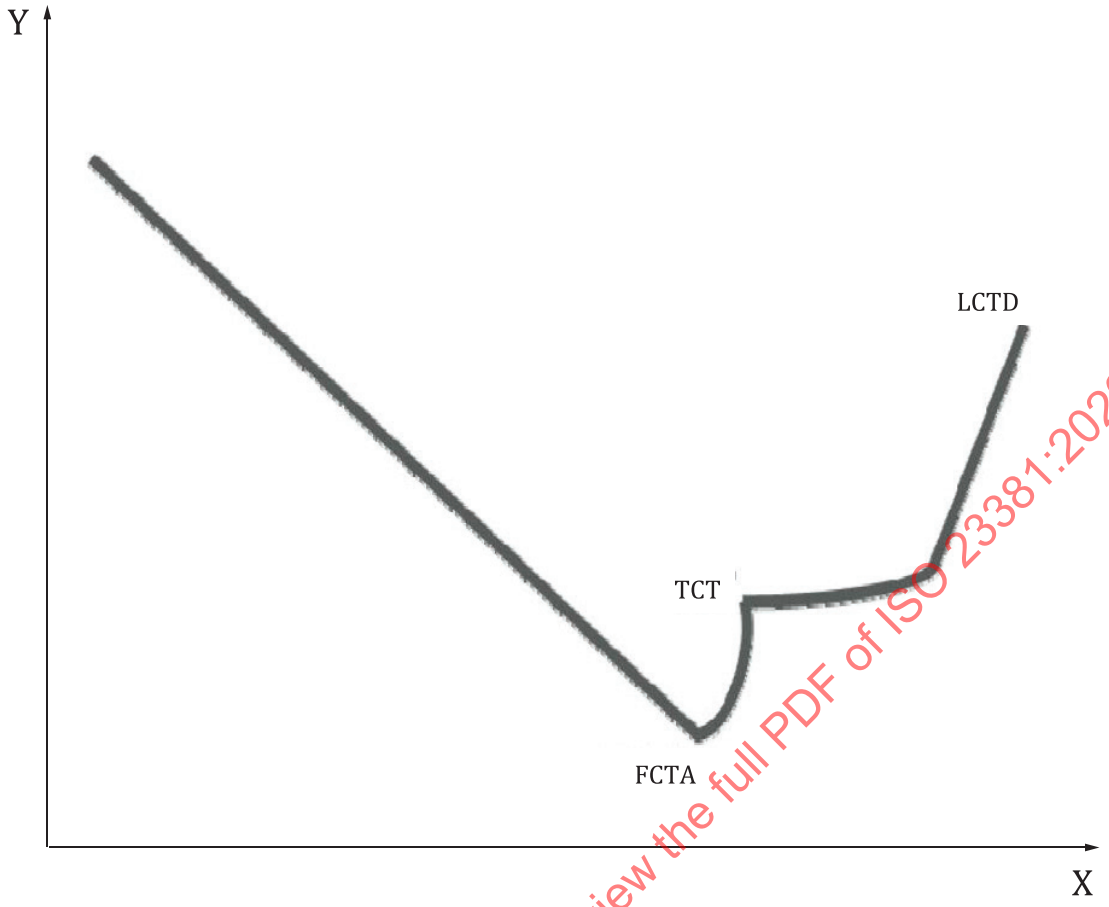
4 Principles

Liquid fertilizers have been defined in ISO 8157:2015.

An aliquot of the original liquid fertilizer sample is placed into a glass test tube and is then immersed into an alcohol-dry ice bath until it crystallizes. The alcohol could be chosen from methanol, ethanol, or isopropanol (IPA). Acetone could also be used instead of alcohols; however, IPA (rubbing alcohol) is preferred due to its higher boiling point. If dry ice is not available, other lowering temperature mixtures such as salt-ice could be used to achieve the proper cooling and crystallization of the fertilizer test sample.

Once the precipitation (formation of salt crystals) is complete, the cooling source is removed and the glass test tube and its contents are allowed to warm up to room temperature. The SOT in most cases is defined when the last crystal to dissolve (LCTD) dissolves (i.e. is no longer visible in the solution). Exceptions to the LCTD rule are covered below and in 8.11.

The underlying principal of the technique can be illustrated with the following cooling curve[9] shown in Figure 1.



Key

X time

Y temperature

Figure 1 — Typical crystallization curve

The first crystal to appear (FCTA) point is the point at which salt crystals start to form. The formation of salt crystals generates a small amount of heat, which causes a slight rise in the solution's temperature. This higher temperature corresponds to the true crystallization temperature (TCT). At this temperature, solids and liquid are present. Once the crystals have formed, the sample is warmed up at ambient temperature until all the crystals are re-dissolved. The point on the curve which corresponds to the temperature at which the last crystal re-dissolves into the solution is called the LCTD[9].

The LCTD might not be applicable to all liquid fertilizers, especially to the binary and ternary systems and other fertilizer blends. In the case that last crystal does not disappear or solid remains in the solution upon warming at ambient temperature, the procedure must be repeated and the SOT should be recorded for the FCTA. This might be applicable to some urea ammonium nitrate (UAN) samples, as well as binary and ternary blends.

5 Reagents

WARNING — Handling dry ice requires the use of insulated gloves to prevent frost bite. IPA, ethanol, methanol, and acetone are flammable and should be used in the absence of open flames. The use of these solvent with dry ice requires that all operations be carried out in an approved chemical fume hood. Add the dry ice in small portions to the solvent to avoid splashes. This document does not point out all possible safety problems, and the user shall bear the responsibility to take proper safety and health measures, and ensure the operations are compliant with the conditions stipulated by the related laws and regulations of the state.

5.1 Use only water conforming to grade 3 of ISO 3696:1987.

5.2 Dry ice snow maker (cone, clamp, ring, and thermal bag), or supply of dry ice.

5.3 CO_2 cylinder with a dip tube for making dry ice (or supply of dry ice).

5.4 IPA or other appropriate solvents such as methanol, ethanol, or acetone.

5.5 If dry ice is not available, other cooling systems such as an ice-salt bath could be used. However, care must be taken to achieve a proper low temperature.

6 Equipment

6.1 1 × stir motor apparatus[1)].

6.2 3-Jaw Keyless Chuck with Arbor[2)].

6.3 1 × 2-foot steel rod with attachable base[3)].

6.4 1 × three-prong clamp.

6.5 2 × Silver-lined Dewar Vacuum Flask with cap[4)].

6.6 50 cm^3 glass test tubes (several, Pyrex or similar quality).

6.7 Thin Stainless steel wire (several inches, such as 40 AWG, 0,079 9 mm, or 30 gauges, 0,010 inch, or 24 gauges, 0,58 mm).

6.8 Thin walled latex rubber tubing (several inches).

6.9 1 × thermometer (−40 °C to a least +30 °C), red liquor preferred for ease of reading. Alcohol filled thermometers are preferred over mercury-in-glass thermometers due to safety concerns with mercury. It is recommended that several alcohol thermometers with different temperature ranges be available.

7 Set Up

7.1 Attach a steel rod to its frim base (lab stand).

1) Glas-Col Model 099A GT31 or 099D GT 21 from glas-col.com, 800-425-7265, or Stir-Pak Dual Shaft Mixer, Cole-Parmer UX-04555-44, 800-323-4340 are examples of suitable products available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of these products.

2) GLS 099D A210101, fits Glas-Col Stirrer Model 099A GT31 099D GT21, Cole-Palmer Stir-Pak Dual Shaft Mixer has already included the Chuck and is an example of a suitable product available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of this product.

3) Strong Lab Stand and support with a rigid base such as support stand with rod, 1000 mm length, 16 mm diameter, 180 mm base width from VWR, Catalogue # 241-0101 and is an example of a suitable product available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of this product.

4) Such as item # 8600-0099, Pope Scientific, 866-636-2487. It is an example of a suitable product available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of this product.

7.2 Attach the stir motor apparatus to the lab stand.

7.3 Remove the stir blade and associate metal shaft from the stir motor. These shall be replaced by the glass thermometer.

7.4 Take a thermometer that reads at least −40 °C and add 1 inch of the thin walled latex rubber tubing to the top (non-bulb) of the thermometer.

7.5 To the bottom 3 inches (bulb end) of the thermometer, coil some stainless steel wire. Ensure that the added wire fits within the glass test tube and does not contact (scratch) sides or bottom of the glass test tube when rotated by stir motor.

7.6 Place the thermometer into where the stir blade rod was before and carefully tighten it around the thermometer.

NOTE If the stir blade rod is tightened too much, the thermometer might break.

7.7 Examples of equipment and set up are shown in Annex A.

8 Procedure

8.1 Pour approximately 250 ml of IPA into the silver-lined Dewar vacuum flask (methanol, ethanol, or acetone can be used as well).

8.2 Pour dry ice snow gently (from dry ice supply or the thermal bag) to the Dewar flask. As the dry ice dissipate, add more. Do not add large pieces of dry ice (crush the dry ice, if large pieces exist).

CAUTION — Dry ice will cause freeze burn. Do not handle with bare hands (use insulated gloves). Dry ice added to IPA (or other aforementioned solvents) creates a bubbly reaction. Add the dry ice slowly.

8.3 Stir the IPA/dry ice mixture with a spatula. Use a variable transformer (variac) connected to the stirrer. Adjust the variac setting in order to provide adequate stirring of about 50-60 RPM (the setting on variac is about 30-40).

8.4 Add 15 ml of the test sample (liquid fertilizer) to the test tube.

8.5 Affix the test tube containing the test sample with a three-pronged clamp and position such that the thermometer end containing the stainless steel wire is placed inside and centred on the test tube. Make sure the thermometer is almost to the bottom of the test tube, but not touching it; this is done to ensure that almost all the forming crystal will mix and not settle on the test tube bottom.

8.6 Make sure the thermometer can rotate and adequately stir the sample in the test tube without touching the sides and the bottom of the test tube.

8.7 Start stirring.

8.8 As the thermometer stirs the solution in the test tube, take the Dewar flask of alcohol/dry ice and place it around the test tube. Make sure all of the tube containing the test sample is immersed fully into the alcohol/dry ice solution to ensure even cooling.

8.9 Cooling the test sample: cooling for 15 s to 20 s, then take out the Dewar flask for 5 s. Repeat this “into flask/out of flask” sequence until all the liquid contents in the test tube precipitate and the

formation of salt crystals is completed. The resulting slurry may slow the stirring action of the rotating thermometer which is acceptable.

8.10 Warming the test sample: remove the Dewar flask containing alcohol/dry ice and while stirring, allow the test tube to warm to room temperature.

8.11 Measurement: record the SOT as the temperature when the last crystal present in the solution is no longer visible.

8.12 Report the SOT in both °F and °C if specified.

8.13 If no precipitate or obvious salt crystals form in the liquid sample when the temperature is −40 °C, report the SOT at < −40 °C.

8.14 If a few solid crystals remain and do not go into the solution at room temperature, report the SOT at that temperature.

8.15 If a large amount of solid remains undissolved, repeat the measurement using a fresh test sample and report the SOT when the first crystal appears.

8.16 In the case of UAN, report the SOT as the first crystal appears upon slow cooling (cooling 1 °C to 2 °C per min).

8.17 Report the SOT as ranges.

Annex A
(informative)

Examples of the equipment and setup

Figure A.1 — Stir Motor and keyless chuck

Figure A.2 — Stir motor and thermometer assembly

Figure A.3 — Thermometer with stainless steel wire

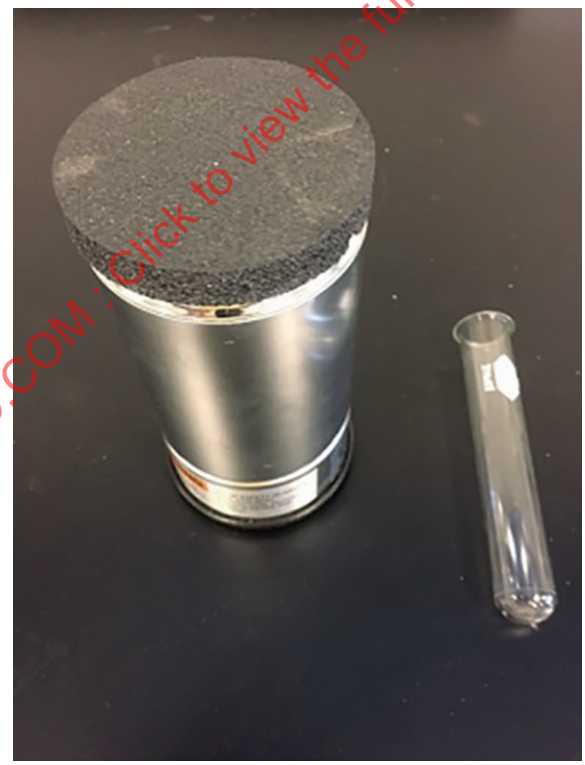


Figure A.4 — Dewar flask and test tube

Figure A.5 — VARIAC

Figure A.6 — Set up with liquid fertilizer for SOT testing