DRAFT INTERNATIONAL STANDARD

ISO/DIS 23381

ISO/TC **134**	Secretariat: **ISIRI**
Voting begins on: **2020-01-03**	Voting terminates on: **2020-03-27**

Determination of Salt Out (Crystallization) Temperature of Liquid Fertilizers

ICS: 65.080

This document is circulated as received from the committee secretariat.

ISO/CEN PARALLEL PROCESSING

Reference number
ISO/DIS 23381:2020(E)

COPYRIGHT PROTECTED DOCUMENT

ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Fax: +41 22 749 09 47
Email: copyright@iso.org
Website: www.iso.org

Published in Switzerland

Contents

Page

Foreword

The International Organization for Standardization (ISO) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committee. 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.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directive, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75% of the member bodies casting a vote.

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.

Introduction

The World liquid fertilizers market was estimated at 11.26 billion dollars in 2015. It is projected to grow at the rate of 3.1% from 2016 to reach 13.48 billion dollars by 20211. 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 Rest of the World at 9%1.

The key manufacturing players are BASF (Germany), E.I du Pont de numerous (US), The Dow Chemical Company (US), Monsanto Company (US), Bayer CropScience AG (Germany), Yara International (Norway), Israel Chemicals Ltd (Israel), and Sociedad Quimica Y Minera SA (SQM) (Chile). The products manufactured by these companies are further used by other fertilizer manufacturers, large agricultural firms, government, and water-soluble fertilizer-related companies such as Hebie Monband Water Soluble Fertilizer Co., Ltd (China), Coromandel International Ltd (India), and The Mosaic Company (US), among others.

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 areal 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.

1.2. 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 should be taken to avoid crystallization.

Accurate crystallization data and an accurate, easy to use, and a universal method for the determination of salt out temperature (SOT) (crystallization temperature) of liquid fertilizers is a helpful reference for stakeholders to avoid or prevent crystallization of these popular fertilizers during the cold season[2].

1.3. Proposal

This international standard specifies the test procedure for determining the salt out temperature (SOT, crystallization temperature) of the liquid (Fluid) fertilizers.

Determination of Salt Out (Crystallization) Temperature of Liquid Fertilizers

1 Scope

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 D11771-17 for the determination of freezing point of aqueous engine coolants, and the ASTM D97 (Pour Point) have also been cited in the literature for Salt Out Temperature (SOT) measurements of liquid (Fluid) fertilizers.

In Addition to these cited methods, ISO (International Organization for Standards) also have set methods to determine the melting/freezing temperature of chemicals. ISO 1392 Method is for the determination of the crystallization point of chemicals, and ISO 3016 Petroleum Oils is for Determination of pour points.

Differential Scanning Calorimetry (DSC) 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. Bothe 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 $50K.

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

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

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 crystallization temperature (CT), or the salt out temperature (SOT) is the temperature at which the last crystal dissolves.

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 3696:1995, *Water for Analytical Laboratory Use- Specification and Test Methods*

*Liquid Fertilizers have been defined in ISO 8157:*2015.

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/

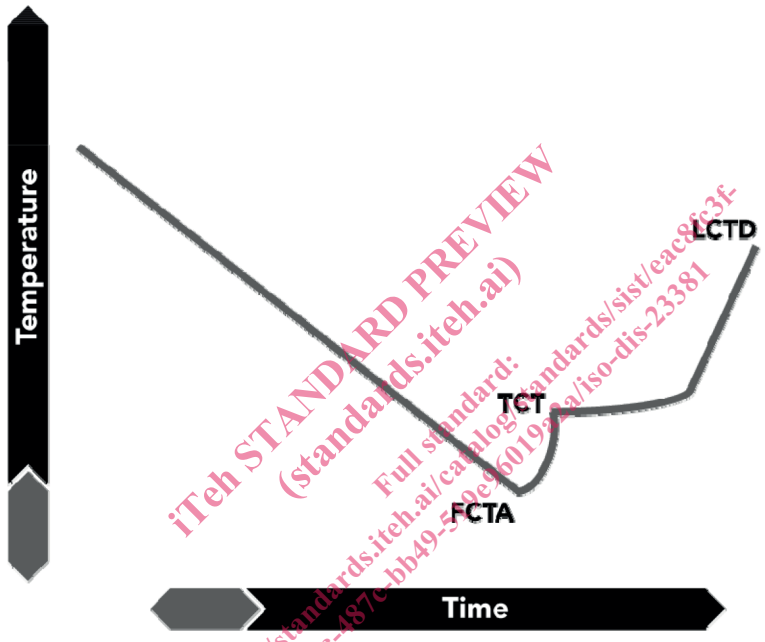
— ISO Online browsing platform: available at http://www.iso.org/obp

4 Principles

An aliquot of the original liquid fertilize sample is placed into a glass test tube and is then immersed into an alcohol-dry ice bath until crystallizes. The alcohol could be chosen from methanol, ethanol, or isopropanol (IPA). Acetone could also be use 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 salt out temperature (SOT) in most cases is defined as when the last crystal (LCTD) dissolves (is no longer visible in solution). There are exceptions to the LCTD rule which would be covered below and in Section 8.11

The underlying principal of the technique can be illustrated with the following cooling curve.



First crystal to appear (FCTA) is the point at which salt crystals first 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 warm 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 *Last Crystal to Dissolve*[3].

The Last Crystal to Dissolve (LCTD) may 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 salt out temperature (SOT) should be recorded for the first crystal to appear (FCTA). This may be applicable to some UAN (urea ammonium nitrate) samples as well.

5 Reagents

Warning: Handling dry ice requires the use of insulated gloves to prevent frost bite. Isopropanol (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 standard 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.

Use only water conforming to grade 3 of ISO 3696:1995.

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

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

5.3 Isopropyl alcohol (IPA) or other appropriate solvents such as methanol, ethanol, or acetone.

5.4 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 x Stir motor apparatus (such as Glas-Col Model 099A GT31, or 099D GT 21, glas-col.com, 800-425-7265, or Stir-Pak Dual Shaft Mixer, Cole-Parmer UX-04555-44, 800-323-4340)

6.2 3-Jaw Keyless Chuck with Arbor (GLS 099D A210101, fits Glas-Col Stirrer Model 099A GT31 099D GT21, Cole-Palmer Stir-Pak Dual Shaft Mixer has already included the Chuck)

6.3 1 x 2 foot steel rod with attachable base (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, Catalog # 241-0101)

1 x three-prong clamp

6.4 2 x Silver-lined Dewar Vacuum Flask with cap (such as item # 8600-0099, Pope Scientific, 866-636-2487)

6.5 50 cc glass test tubes (several, Pyrex or similar quality)

6.6 Thin Stainless steel wire (several inches, such as 40 AWG, 0.0799 mm, or 30 gauges, 0.010 inch, or 24 gauges, 0.58 mm).

6.7 Thin walled latex rubber tubing (several inches)

6.8 1 x 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).

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 will 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.