"Screening Test for Thermal Stability and Stability in Air"

(Accelerated Storage Test [CIPAC-Test] - Thermal Analysis Methods, including differential thermal analysis [DTA] and thermogravimetric analysis [TGA])

1. INTRODUCTORY INFORMATION

• **Guidance information**

– Structural formula
– Vapour pressure curve
– Melting point
– Boiling point

• **Qualifying statement**

The test methods can be applied to pure and commercial grade substances. The potential effects of impurities on results must be considered.

• **Standard documents**

This Test Guideline is based on the

– CIPAC-recommendations (4) for stability testing of pesticides (short time storage test); and on
– consensus methods of thermal analysis (DTA, TGA).

2. METHOD

A. INTRODUCTION, PURPOSE, SCOPE, RELEVANCE, APPLICATION AND LIMITS OF TEST

The purpose of the methods is to obtain a preliminary judgement of the stability of a substance with respect to heat and air in order to provide guidance in the performance of other tests.

The methods for determining storage stability discussed in this Test Guideline are applicable to homogeneous solid and liquid substances and to mixtures of these.

Exothermic decomposition processes can be determined by differential thermal analysis (DTA). In order to determine endothermic effects it must be confirmed that it is a decomposition and no phase transition.

Users of this Test Guideline should consult the Preface,
in particular paragraphs 3, 4, 7 and 8.

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The thermogravimetric analysis (TGA) determination gives information about decomposition reactions involving the elimination of volatile decomposition products.

With a TGA kinetic evaluation and extrapolation to lower temperatures may be easier than with DTA.

- Definitions and units (1,2,3)

– Thermal analysis (TA): General term describing analytical methods in which the changes in the physical parameters of a substance as a function of temperature are measured.

– Differential thermal analysis (DTA): Measurement of the temperature difference between a sample and the reference material as a function of time or temperature.

– Thermogravimetric analysis (TGA): Measurement of the weight change of a substance using an isothermal or anisothermal procedure as a function of time or temperature.

– Peak: The term "peak" describes the upward or downward deviation of the recording curve from the base line.

– Peak temperature: Temperature at the peak maximum.

- Reference substances

Suitable reference substances are urea, 4-nitrosophenol, α-naphthylamine and naphthalene. These substances need not be employed in all cases when investigating a new substance. They are provided primarily so that calibration of the method may be performed from time to time and to offer the chance to compare the results when another method is applied.

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• <u>P r i n c i p l e   o f   t h e   t e s t   m e t h o d s</u>

Accelerated storage test (CIPAC)

A long duration storage instability can be simulated by applying a higher temperature during a short test. Such a "screening test" is described in the CIPAC - recommendations (4) for stability testing of pesticides. This test calls for the controlled storage at 54°C to 55°C for 14 days and subsequent analysis. In simple cases it will be enough to determine a characteristic property (e.g. melting point) before and after storage.

Thermal analysis methods

The sample and the standard reference material are heated up to the final temperature at a constant rate in a defined test atmosphere, either separately in a TGA or DTA apparatus or in a combined system, and the weight change of the sample or the quantities of heat absorbed or given off are measured and recorded. If, in the temperature range investigated, peaks are observed from which a chemical reaction of the sample can be deduced, the thermal analysis should be repeated in the immediate vicinity of the peak temperature.

• <u>Q u a l i t y   c r i t e r i a</u>

Repeatability

DTA and TGA are well-known methods for determining thermal stability of chemical compounds. (See Section on accuracy, below).

Sensitivity

The sensitivity of the method is determined by the sensitivity of the measurement apparatus (equipment type) and the test conditions.

Possibility of standardisation

Standardisation of the test conditions for thermal analysis is described by McAdie (5).

Possibility of automation

There is some possibility for automation.

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B. DESCRIPTION OF THE TEST PROCEDURES

- A c c e l e r a t e d   s t o r a g e   t e s t
  (based on CIPAC - Test)

    Apparatus

– Oven, thermostatically controlled
– Sample containers (250-ml beakers, glass bottles, sealable ampoules).

    Procedure

Place 20 g of the sample in a bottle. If the substance is vdatile place in a sealable ampoule. Water saturated air should be used as test atmosphere. Seal the sample container hermetically and keep it in the oven at $55 \pm 2°C$ for 14 days. Remove the sample container from the oven, cool down to room temperature, and determine by a suitable method (e.g. determination of melting point) whether decomposition or other chemical transformation has occurred.

- D i f f e r e n t i a l   t h e r m a l   a n a l y s i s   (DTA)   a n d
  d i f f e r e n t i a l   s c a n n i n g   c a l o r i m e t r y   (DSC)

    Apparatus

DTA or DSC apparatus of commercially available type. (Block diagram of DTA apparatus: Figure 1).

Heat flow and energy compensated methods may both be applied. For volatile substances an apparatus should be available which allows measurements to be performed with closed sample containers or under elevated pressure.

    Test conditions

Sample containers of different kinds may be used: open or sealed glass tubes, metal pans, or pressure resistant crucibles. For measurements under oxygen-containing atmosphere only open sample containers are appropriate.

The test atmosphere is (a) nitrogen and (b) air. When air is used the sample is put in an open pan.

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Figure 1: Block diagram of a DTA apparatus
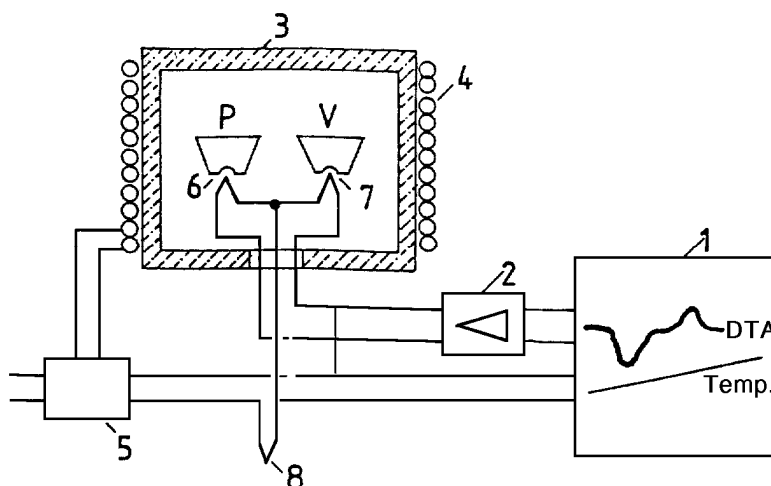
1   Two-channel recorder
2   D.C. amplifier
3   Furnace
4   Heater windings
5   Temperature regulator
6   Thermocouple with crucible P for sample substance
7   Thermocouple with crucible V for reference substance
8   Reference junction thermocouple

An inert reference substance is selected which undergoes no changes in the temperature region employed. Thermal conductivity and heat capacity of the inert reference sample should be nearly equal to those of the sample to be investigated. In many cases aluminium oxide is a useful inert substance.

Procedure

Samples of about 5 to 50 mg are weighed and closed in the sample container. The heating rate should be in the range of 2 to 20 K/min. At first a DTA diagram (for example see Figure 2) of the substance at normal pressure is recorded.

If a thermal effect (a peak) is found between room temperature and 150°C, one proceeds as follows:

(a)   When the peak is due to an exothermic effect, it is assumed to be a decomposition.

(b)   When the peak is due to an endothermic effect, the temperature at which it occurs should be compared to the melting point of the substance.

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Figure 2: DTA curve
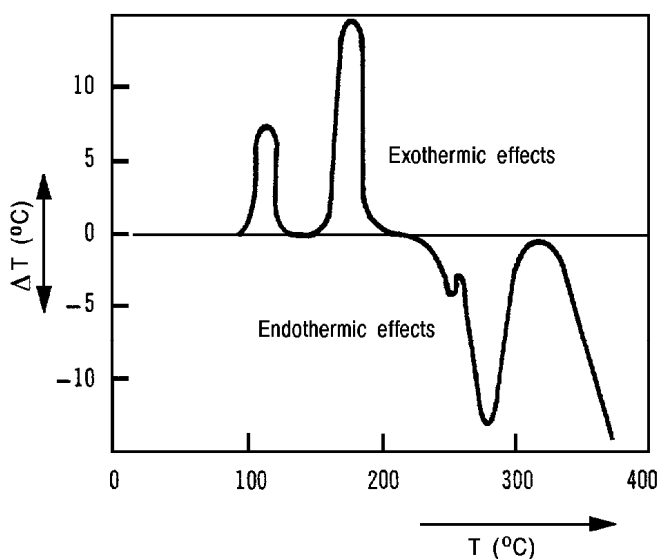
T : temperature of the reference substance.

ΔT : temperature difference between sample and reference substance.

(c)   If the peak is due to an endothermic effect which is not related to the melting of the substance, the DTA should be repeated at a higher pressure (10-50 bar) or in a closed sample container. If the peak is shifted to a higher temperature, it comes from a vaporisation process.

(d)   If the endothermic effect is due neither to melting nor to vaporisation, repeated heating cycles are carried out around the peak temperature. If the peak does not persist a chemical transformation has occurred.
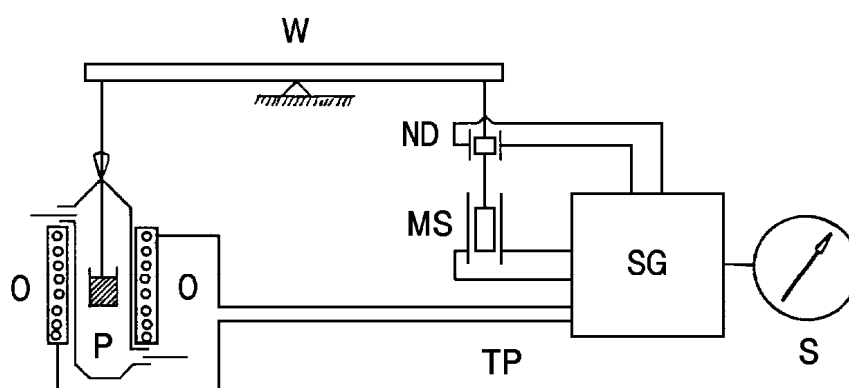
• Thermogravimetric analysis (TGA)

Apparatus

TGA Apparatus of common design, e.g. of commercially available type, allowing for heating the substance in air and in an inert atmosphere. (Diagrammatic sketch of the apparatus: Figure 3.)

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Figure 3: Diagrammatic structure of a TGA apparatus

W	Balance beam	ND	Zero detector
P	Sample	MS	Magnet coil (weight compensation)
O	Furnace	SG	Control unit
S	Recorder	TP	Temperature programming

Test conditions

The test atmosphere is normally (a) nitrogen and (b) air. For testing oxidation stability air is used as atmosphere.

Procedure

A sample of about 10 to 500 mg is heated in (a) nitrogen and (b) air, and the weight loss is recorded. The heating rate should be in the range of 2 to 20 K/min. A weight loss which does not originate from volatilisation of the substance is considered as a decomposition.

If a decomposition is observed at temperatures below 150°C the rate of decomposition can be determined by isothermic measurements.

3. DATA AND REPORTING

• Interpretation of results

The substance is considered to be stable at room temperature if either

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a)   in the "Accelerated Storage Test (CIPAC-Test)" the melting point (or another characteristic property) has remained constant or if the content of original substance as determined by analysis has decreased by not more than 5 per cent

or

b)   in DTA or TGA no decomposition or chemical transformation is found below 150°C.

- T e s t   r e p o r t

    The test report should contain the following information:

Accelerated storage test

– Type of sample container

– Method of determination of a chemical transformation

– Change of a typical property or percentage of decomposition after 14 days' storage.

Thermal analysis

– Type of apparatus employed

– Preliminary treatment and form of the sample

– Precise information on reference and test substances

– Temperature range investigated, rate of temperature increase, temperature specifications for isothermal procedure

– Quantity of substance

– Composition and purity of the test atmosphere

– Type of sample container

– Changes observed on the treated sample during and after testing

– Temperature of beginning chemical transformation

– Conditions deviating from this method

– Where possible, report nature of decomposition products.

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