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**Chemically-induced ultra-  
weak photon emission (UPE) —  
Measurement as an analysis method of  
degradation of polymeric material**

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## Foreword

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# Chemically-induced ultra-weak photon emission (UPE) — Measurement as an analysis method of degradation of polymeric material

## 1 Scope

This document provides a method for assessing the very early oxidative degradation state of polymers during outdoor weathering and indoor accelerated weathering tests and the influence of various additives can also be evaluated.

This method is based on an analytical method in which the degree of progress of the oxidative degradation reaction of a polymer is sensitively detected by measurement of chemically induced ultra-weak photon emission (UPE).

## 2 Normative references

There are no normative references in this document.

## 3 Terms and definitions

For the purpose of this document, the following terms and definitions apply.

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

- ISO Online browsing platform: available at <https://www.iso.org/obp>
- IEC Electropedia: available at <http://www.electropedia.org>

### 3.1

#### ultra-weak photon emission

##### UPE

phenomenon of light emission observed when electrons are excited to at least one-level higher energy level due to the energy produced by chemical reaction and then are deactivated from the higher energy levels to the ground state

Note 1 to entry: UPE is often used synonymously with “chemiluminescence”. “Chemiluminescence” means luminescence accompanied with a chemical reaction.

### 3.2

#### dark current value

numeric data measured in a state where the detection element is not irradiated with light

### 3.3

#### background

numeric data measured in a state where samples are not placed in a sample container

### 3.4

#### oxidation induction time

##### OIT

time when the emission intensity rapidly increases due to the disturbance of the equilibrium between the generation rate and the disappearance rate of the peroxide produced in plastics

Note 1 to entry: The oxidation induction time varies according to the type of antioxidant, additive concentration, measurement temperature, ageing status, etc.

### 3.5 gate time

duration over which the incoming photon flux of UPE is accumulated

Note 1 to entry: Typically values between 0,1 s and 10 s are chosen.

## 4 Measurement principle and its limitations

Ultra-weak photon emission (UPE), generated when peroxide formed in an oxidation reaction is decomposed by heat or other stimulators, is measured with an apparatus using highly sensitive photodetection elements (e.g. photomultiplier tube or CCD camera). The time course of UPE intensity is indicated by a measurement of peak height, inclination, time, peak area, light emission image, etc. While the UPE is proportional to the reaction rate of the chemiluminescent oxidation reaction (i.e. the kinetics of the reaction), its time-integrated curve is proportional to the amount of oxidation products formed.

The details of the measurement of UPE of substances and the view of oxidation deterioration are given in [Annex A](#). Values given in [Table 1](#) are reported as the emission wavelength range of emitting species in general chemical reactions.

**Table 1 — Emission wavelength range and peak wavelength of emitting species (chemical material species) in general chemical reactions (example)<sup>[1]</sup>**

Emitting species	Emission wavelength <sup>a</sup> nm
3-aminophthalic acid	350 to 550 (425)
N-methyl acridone	400 to 600 (470)
Dibenzoylbenzoamide	520 to 590 (530)
<sup>1</sup> O <sub>2</sub>	420 to 720 (478, 634)
Excitation carbonyl	420 to 450 (530)
HCHO	300 to 600 (435)
NO <sub>2</sub>	540 to 3 000 (1 200)
SO <sub>2</sub>	250 to 400 (312)
<sup>a</sup> The numerical values in parentheses indicate peak wavelength (maximum wavelength).	

The method is very useful to follow the ageing process of a polymer with the photon emission being measured as a relative value of the oxidation products. However, the photon emission of the considered material depends on a lot of effects, which can change during ageing and differ for various materials, such as surface of the material and its absorption, or the depth from which photons reach the surface.

NOTE The method can be used to probe the residual stabilization or oxidation state of the material, subsequent to a stepwise weathering exposure.

The method is a relative comparison method and cannot give an absolute measure of a materials ageing status.

## 5 Sample

Weigh out 10 mg to 20 g of the sample with a weighing apparatus capable of measuring 1 mg at least. Among samples all made of the same composition of plastics, choose samples that differ in either one of the conditions (e.g. degree of deterioration, additive agent type or additive amount), and weigh out the same mass of each sample. For a solid sample, the sample area shall also be the same. The shape, dimension and mass of the sample shall be as agreed between the customer and the manufacturer.

Handle the sample with gloves, not with bare hands. Remove any soil on the sample entirely before measurement.

NOTE Since UPE intensity is theoretically proportional to the surface area of a sample, the absolute value of samples in the same shape can be compared among samples, but the absolute value of UPE for samples in different shapes cannot be compared.

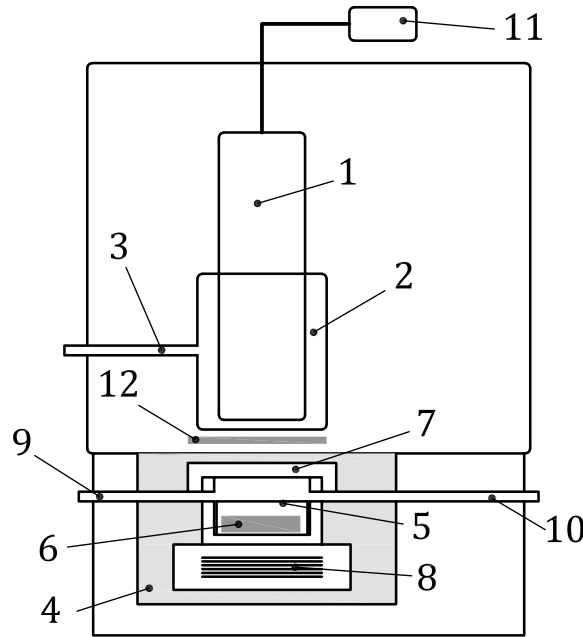
## 6 UPE measuring apparatus

### 6.1 Composition of UPE apparatus body

The body of the UPE measuring apparatus (hereafter referred to as UPE apparatus) shall be capable of controlling the addition of heat to the sample and of selecting the atmosphere. For the temperature, the UPE apparatus shall have the structure that allows to perform isothermal measurement and/or non-isothermal measurement. For the light receiving section which detects UPE from the sample, highly sensitive detection elements (e.g. photomultiplier and highly sensitive CCD camera) shall be used. The detection element shall be capable of detecting the light emission of the peroxide under measurement. Since the cooling of a detection element increases the sensitivity, the detection element should be cooled down and kept lower than 0 °C. The sample chamber shall be located directly under the detection element, and UPE shall be generated by decomposing the peroxide in the sample by heating. An example of the composition of an UPE apparatus body is shown in [Figure 1](#). The data processing device should be capable of measuring light emission amount as a numerical value (e.g. light emission count value) and of displaying the time-course of light intensity temporal change on a monitor display. Furthermore, for a certain level of strong light incident on a detection element, the UPE apparatus shall have a function of suspending the measurement by, for example, closing a shutter automatically for the protection of the detection element. The measurement (upper) limit value of the detection element shall be set by the detection element manufacturer or the UPE apparatus manufacturer.

### 6.2 Composition of sample chamber

The sample chamber shall consist of a gas inlet and outlet and a heating section, and the inside of the sample chamber shall be sealed with an inner lid with an aperture plate. The aperture plate shall be made of quartz glass normally, that does not inhibit light emission and have high permeability. The sample container shall have a flat bottom and fixed open area. The sample container shall be made of a material that has high thermal conductivity and very low level of light emission, such as stainless steel and aluminium. The anticorrosion container such as a glass container and ceramic container may be used depending on the measurement purpose. The sample chamber shall have a function of introducing and discharging inert gas such as nitrogen and/or oxidation accelerating gas such as oxygen.



**Key**

- |   |                            |    |                               |
|---|----------------------------|----|-------------------------------|
| 1 | photomultiplier tube (PMT) | 7  | inner lid with aperture plate |
| 2 | electron cooling           | 8  | heating section               |
| 3 | cooling water              | 9  | gas introduction tube         |
| 4 | sample chamber             | 10 | gas exhaust tube              |
| 5 | sample container           | 11 | data processing               |
| 6 | sample                     | 12 | shutter                       |

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**Figure 1 — Composition of an UPE apparatus body (example)**

**6.3 Installation environment for UPE apparatus**

The installation environment for an UPE apparatus shall have the following characteristics:

- a) a place not exposed to direct sunlight (photo darkroom is recommended);
- b) a place not exposed to strong ultraviolet radiation, electromagnetic waves or vibration;
- c) a place where an UPE apparatus is not affected by dust, soot, etc. containing chemical agents;
- d) a place where indoor temperature can be kept constant (about 20 °C to 25 °C is recommended);
- e) a place where indoor humidity can be maintained constant (the humidity of about 45 % to 65 % is recommended);
- f) a place where the UPE apparatus can be installed far away from the air outlet of an air conditioner;
- g) a place where a general precision analytical instrument is installed.

**6.4 Sensitivity check**

Regularly, there are two ways to check the sensitivity.

- a) Sensitivity check of detection elements (e.g. PMT or CCD camera)
  - 1) Prepare the calibrated source which should be as constant in its emission as possible over time or its time dependence should be extremely well repeatable and reproducible and documented.



- 2) The calibrated source can be a material which shows UPE, or a ready assembled unit such as LED elements with diffusion plate on top. Ideally, the calibration source should be in the range of about the emission level(s) to be detected in the following measurements.

- b) Sensitivity check for the UPE system [see 7.3.2 f)]

Measure UPE with an empty sample container and compare with the normal background level. The check process should ideally start any new measurement series as for instance condensation products from samples measured earlier can contaminate the optics and reduce the emission detected.

NOTE This sensitivity check, at least, allows making a semiquantitative comparison of measurements in terms of relative amount of products formed (relative emission axis) within one sequence of sensitivity check and subsequent measurement cycle.

## 7 Measurement method

### 7.1 UPE apparatus preparation

- a) Start the cooling function of the UPE apparatus, if it is installed, and check that the circulation of cooling water is working properly.
- b) Start the UPE apparatus and wait until the detection element is stabilized.

### 7.2 Confirmation of normal operation of UPE apparatus

Measure the dark current value and confirm that the value is within the normal range specified by the manufacturer.

### 7.3 Measurement procedure

#### 7.3.1 Setting of measurement condition

Determine atmosphere, temperature, gate time and measurement time which are optimal for measurement as follows.

- a) Measurement atmosphere: Select the atmosphere of inert gas or oxidation accelerating gas.

NOTE 1 Typical inert gas is nitrogen or argon. The sample is not oxidized during the measurement in an inert gas; therefore, the state of oxidation can be detected.

NOTE 2 Examples of oxidation accelerating gas are oxygen, air and ozone. In the oxidation accelerating gas, the sample is oxidized during the measurement, then, the resistance to oxidation of the sample can be evaluated.

The atmosphere may be changed during measurement according to the purpose. Certain type of atmosphere gas can affect the heating control of the sample chamber.

- b) Measurement temperature: Set the optimal temperature according to the measurement purpose in consideration of the physical information (glass transition, melting, and decomposition temperature) of a sample. The temperature shall be controlled by the following two methods, which can be applied in combination.
- 1) Isothermal measurement: Maintain the temperature of the sample chamber at the predetermined temperature beforehand and perform the measurement at the predetermined temperature from the start until the end of the measurement.
  - 2) Non-isothermal measurement: Perform the measurement while raising the temperature from low temperature (around room temperature) to the predetermined temperature at a constant rate (approximately 1 °C/min to 150 °C/min).

Measurement temperature should be as low as possible compared to the application conditions of the sample material or correlation is lost. Especially, phase transitions and glass temperature should not occur in the comparison of experiment's temperature range and application temperature range. On the other hand, this temperature level should be high enough to achieve a suitable signal to noise ratio of UPE.

- c) Gate time: In general, it is set within 0,1 s to 10 s. When the emission intensity is low, it is better to set longer, such as within 1 min to 5 min.
- d) Measurement time: Set the time from the start of measurement of UPE until the end.

NOTE 3 When the measurement is performed in an inert gas atmosphere, light emission often reaches its peak approximately in 5 min to 1 h.

NOTE 4 When the measurement is performed in an oxidation accelerating atmosphere, light emission often reaches its peak in, approximately, several hours to several days.

### 7.3.2 Measurement of background

The measurement of a background shall be as follows.

- a) When gas is used as measurement atmosphere, fill the sample chamber with the gas beforehand. Change the gas flow rate according to the capacity of the sample chamber. The flow rate should be measured and controlled, for example, 50 ml/min to 150 ml/min, for an about 40 ml sample chamber.
- b) For the isothermal measurement, set the temperature of the sample chamber to measurement temperature, and wait until the temperature is stabilized at the preset temperature. For the non-isothermal measurement, set the measurement start temperature, temperature rise rate and target temperature, and wait until the temperature is stabilized at the measurement start temperature.
- c) Set the gate time and measurement time. The measurement time should be the same as the time for actual sample measurement.
- d) When the temperature is stabilized, put an empty sample container into the sample chamber, and close the inner lid with an aperture plate to seal the inside. When gas is used as measurement atmosphere, a gas discharge monitor should be connected to the piping connected to the gas outlet.
- e) Start the measurement.
- f) When an abnormally high light emission is observed compared with the light emission amount before measurement, the sample container or other parts could be soiled; therefore, clean the surrounding of the sample chamber and exchange the sample container.

### 7.3.3 Sample measurement

- a) Set the same measurement condition as the condition for background measurement.
- b) Put the sample into the sample container, install the sample container in the sample chamber, and attach the inner lid with an aperture plate.
- c) When gas is used as measurement atmosphere, confirm that gas is surely charged into and discharged from the sample container.
- d) Start the measurement.
- e) After the measurement, open the inner lid with an aperture plate using heat resistant gloves, and take out the sample. Wash the inside of the sample chamber and the inner lid with an aperture plate, if being soiled.
- f) Check the measurement data (e.g. light emission count value, peak value, integrated value and light emission after a lapse of a fixed time) of each sample.

- g) When the measurement results indicate that the degree of oxidation deterioration has not been evaluated as intended, re-examine the temperature condition and atmosphere condition, and repeat the measurement from the beginning.

NOTE 1 The measured UPE intensity includes the background. Therefore, the UPE intensity from the sample is the intensity obtained by subtracting the background from the measured value of UPE intensity.

NOTE 2 When a sample absorbs light, the result with an unoxidized sample can be used as background data.

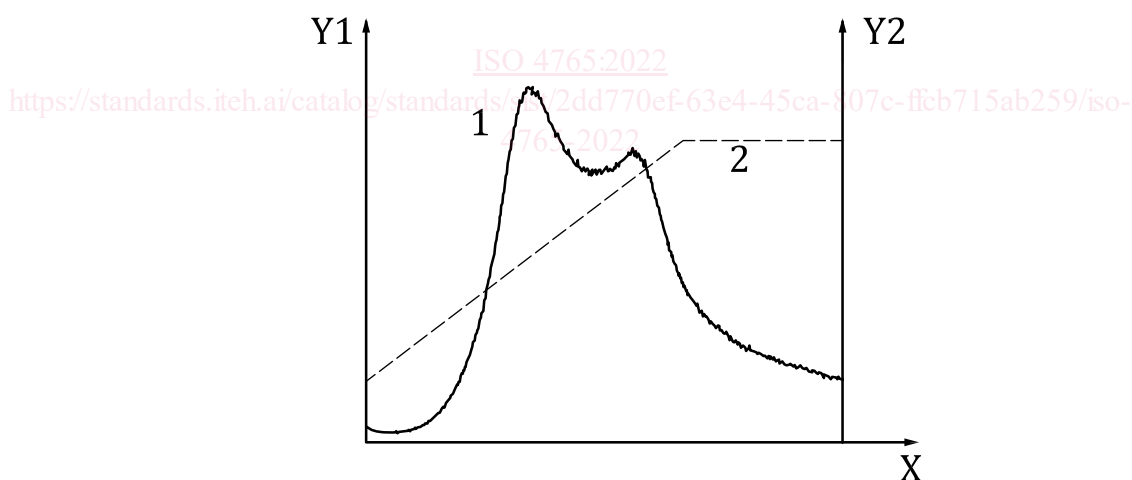
## 8 Display of measurement results

### 8.1 General

The measurement temperature condition (isothermal measurement or non-isothermal measurement) and the atmosphere condition (inert gas atmosphere or oxidation accelerating atmosphere) inside the sample chamber are set, and the emission intensity is measured. Then, the measurement results are displayed. The time-course of emission intensity is illustrated in 8.2 and 8.3. Examples of UPE measurement of polypropylene (PP) and polyethylene (PE) materials are given in Annex B and Annex C. Examples of measurement of OIT of PP materials with different antioxidant concentration are given in Annex D. Examples of UPE measurement of PP oxidized by an accelerated weathering test are given in Annex E.

### 8.2 Measurement in inert gas atmosphere

- a) Non-isothermal measurement: The emission intensity generally changes with passage of time as shown in Figure 2. Light is emitted when the temperature reaches the point where peroxides or other components in a sample react.



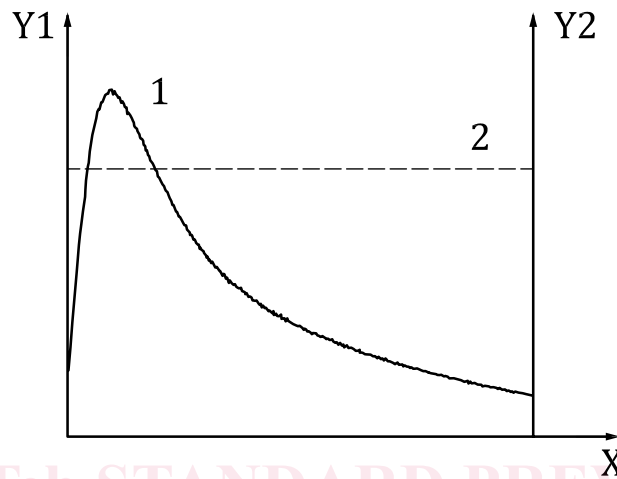
#### Key

- X time  
 Y1 emission intensity  
 Y2 temperature  
 1 emission intensity curve  
 2 sample chamber temperature

**Figure 2 — Time course of emission intensity for non-isothermal measurement in inert gas atmosphere (example)**

NOTE 1 The peak can appear more than once due to two or more components contained in a sample which react at different temperatures. Phase change such as crystallization, melting and phase separation of the sample, viscosity change, are the other causes of multiple peaks in the non-isothermal measurement.

- b) Isothermal measurement: The emission intensity generally changes with passage of time as shown in [Figure 3](#). The light emission is derived from the peroxide which exists in a sample, and the light emission amount is equivalent to the degree of oxidation deterioration at the time of start of measurement. After the light emission amount reaches its peak, it decreases. For a sample of a thin film which conducts heat quickly, the light emission peak may appear before measurement. In this case, the measurement temperature is required to be re-examined, such as lowering the measurement temperature, for example.



**Key**

- X time
- Y1 emission intensity
- Y2 temperature
- 1 emission intensity curve
- 2 sample chamber temperature

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**Figure 3 — Time course of emission intensity for isothermal measurement in inert gas atmosphere (example)**

NOTE 2 From the peak(s) in non-isothermal measurements, the information of the temperature range at which the chemical reactions related with UPE becomes dominant can be obtained. Referring to this peak temperature in non-isothermal measurement, it is possible to determine the temperature of isothermal measurement.

**8.3 Measurement in oxidation accelerating atmosphere**

- a) Non-isothermal measurement: With this measurement, the information of the temperature of the oxidation initiation is obtained. A typical emission intensity change with passage of time is shown in [Figure 4](#).

NOTE 1 The peak can appear more than once due to the multiple components contained in a sample which react at different temperatures. Phase change such as crystallization, melting and phase separation of the sample, and viscosity change with temperature rising can be also the cause of multiple peaks.