INTERNATIONAL STANDARD

ISO 4765

First edition
2022-04

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

Reference number
ISO 4765:2022(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 61, *Plastics*, Subcommittee SC 6, *Ageing, chemical and environmental resistance*.

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.

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)[1]

Emitting species	Emission wavelength [a] nm
3-aminophthalic acid	350 to 550 (425)
N-methyl acridone	400 to 600 (470)
Dibenzoylbenzoamide	520 to 590 (530)
$^1O_2$	420 to 720 (478, 634)
Excitation carbonyl	420 to 450 (530)
HCHO	300 to 600 (435)
NO_2	540 to 3 000 (1 200)
SO_2	250 to 400 (312)

[a] 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.

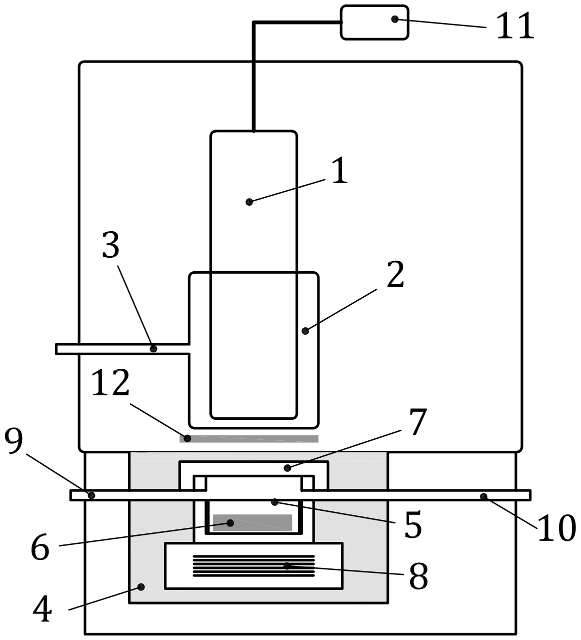
6 UPE measuring apparatus

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

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 ration 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.

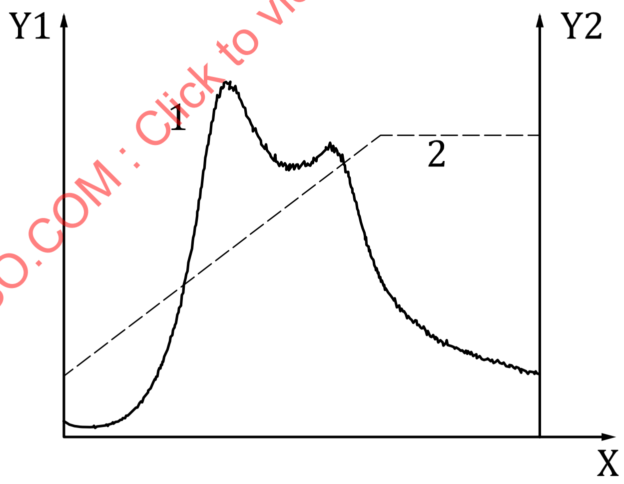
8 Display of measurement results

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

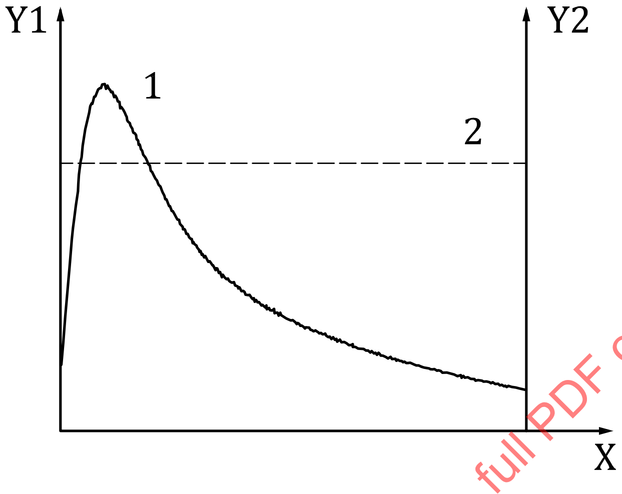
1 emission intensity curve

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

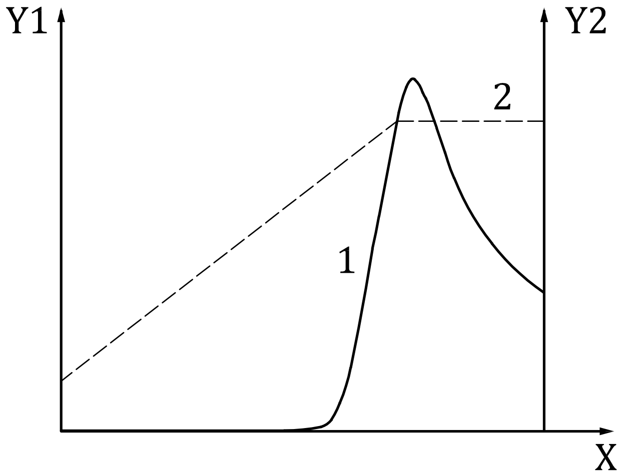
Figure 3 — Time course of emission intensity for isothermal measurement in inert gas atmosphere (example)

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.



Key

X time

Y1 emission intensity

Y2 temperature

1 emission intensity curve

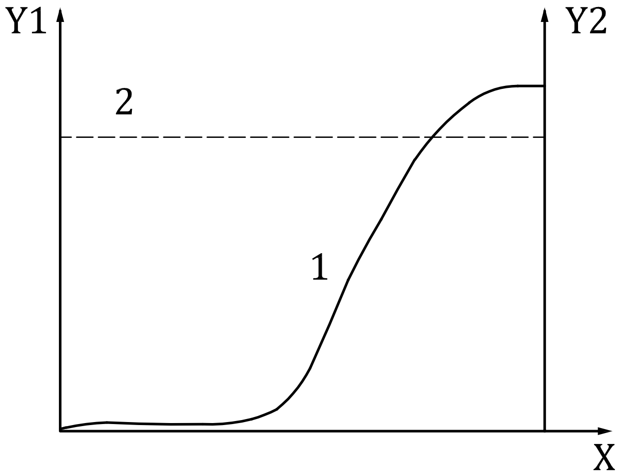
2 sample chamber temperature

Figure 4 — Time course of emission intensity for non-isothermal measurement in oxidation accelerating atmosphere (example)

b) Isothermal measurement: The emission intensity generally changes with passage of time as shown in Figure 5. The first light emission peak is achieved by the same factors as in the case of the measurement in inert gas atmosphere. After the generation rate and disappearance rate of the peroxide produced in the sample are kept in equilibrium for some period of time, the equilibrium is broken, and the emission intensity increases rapidly. The emission intensity in equilibrium indicates the stability of materials and the effectiveness of the stabilizer added.

For some cases, a rapid increase of emission is observed before a distinct equilibrium. In that case the measurement conditions should be re-examined to catch OIT clearly.

NOTE 2 OIT indicates the ease of oxidation and the effectiveness of a stabilizer and is used as an index for predicting the end of life caused by deterioration by heat.



Key

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

Figure 5 — Time course of emission intensity for isothermal measurement in oxidation accelerating atmosphere (example)

9 Test report

The test report shall contain at least the following:

a) the number of this document, including the year of publication, i.e. ISO 4765:2022;

b) test date;

c) testing UPE apparatus (e.g. model number);

d) test conditions (e.g. temperature condition and atmosphere);

e) information on sample (e.g. sample type, additive agent, shape, mass, and oxidation and heat history of sample);

f) information on sample container (e.g. size, opening area and material);

g) temporal change data or graph of emission intensity;

h) temporal change data or graph of sample chamber temperature;

i) other items agreed between the customer and the manufacturer.

Annex A
(informative)

Detection of oxidation deterioration by UPE measurement

A.1 Oxidation deterioration and principle of UPE

Various luminescent phenomena are shown in Figure A.1. Naked eyes are capable of detecting light such as stars and fireflies, but not ultra-weak photon emission (UPE) resulting from the behaviour of light as a particle (photon). The phenomenon of light emission caused by the chemical reaction of oxidation and/or deterioration of organic substances such as food, oil, plastics and rubber are called UPE. Using the method of UPE detection, ultra-low volume of oxidation reaction can be detected at each stage of material quality control, production process control, additive effect, product life prediction, and reuse and recycling quality control.

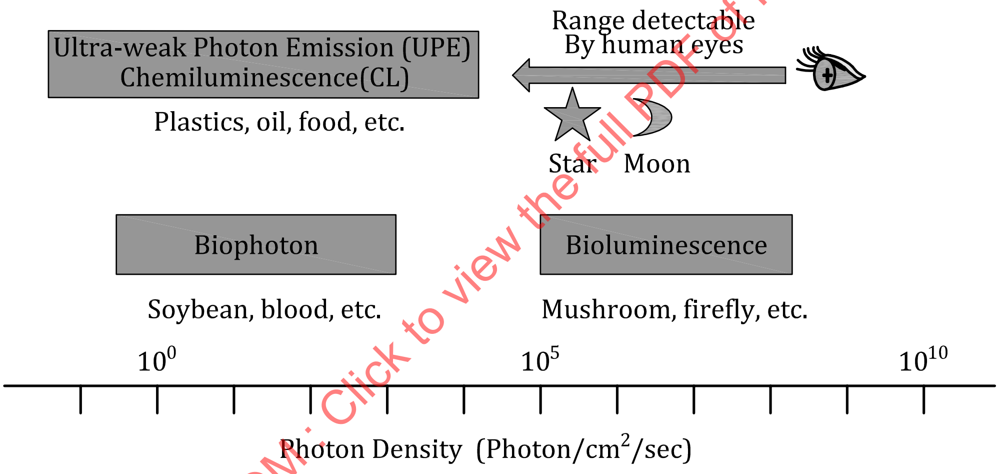


Figure A.1 — Luminescent phenomena of various substances

Under the UPE method, which does not require a light source, light is highly sensitively detected from the sample placed in the pitch-dark sample chamber. For this reason, the photodetection is free from stray light or an increase in background caused by a light source and has a high signal/noise (S/N) ratio compared with other photodetectors (e.g. UV-visible spectrophotometer, infrared spectrophotometer and spectrophotofluorometer), and therefore highly sensitive detection becomes possible.

The occurrence of UPE is considered to be mostly derived from the peroxide produced by the oxidation reaction of organic substances. The mechanism of light emission of organic substances due to oxidization has been known to be part of autoxidation mechanism for a long time. The main chemical reaction part in the autoxidation mechanism is shown in Figure A.2. Unoxidized polymer (RH) produces an alkyl radical by a stimulus of light, heat, etc. This radical reacts with oxygen to form a peroxy radical ($ROO^{\bullet}$) promptly, and then becomes peroxide (ROOH). ROOH decomposes and becomes $ROO^{\bullet}$ again. This bimolecular reaction produces excited carbonyl in a high energy state and singlet oxygen which is one of active oxygen. When these fall onto the ground state from the excited state, the energy difference is emitted as light. This is defined as UPE (Reaction 1). This process in an autoxidation mechanism is also called Russell mechanism. The production amount of ROOH, i.e. the degree of oxidation deterioration, is measured by detecting this UPE. This is the UPE method, and the measured value is expressed as a light emission amount. In ordinary cases, ROOH is decomposed by heating a sample, and an ultralow volume of ROOH produced and accumulated in the sample is detected. As shown in Reaction 2, the advance of oxidation cuts a molecular chain, resulting in a decrease in molecular weight.

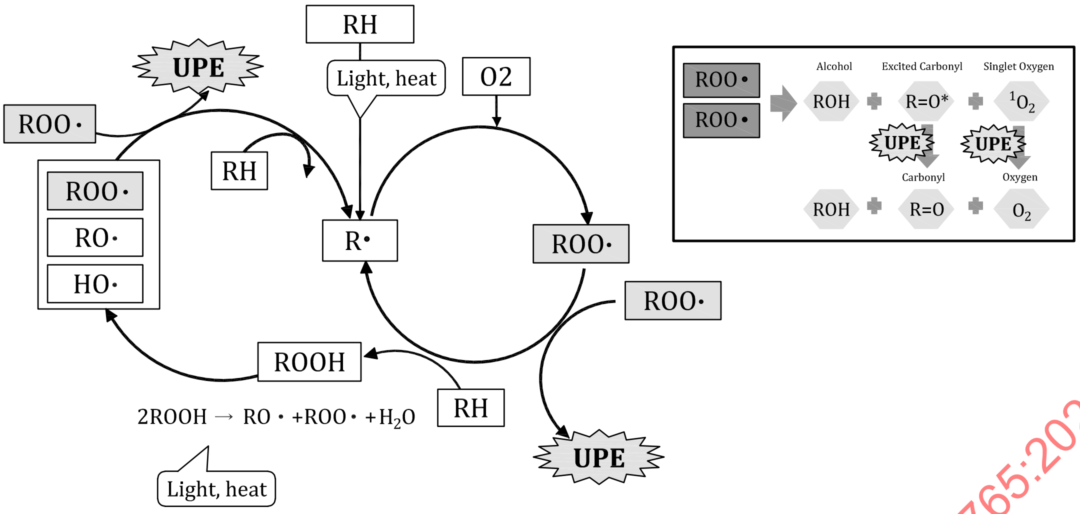
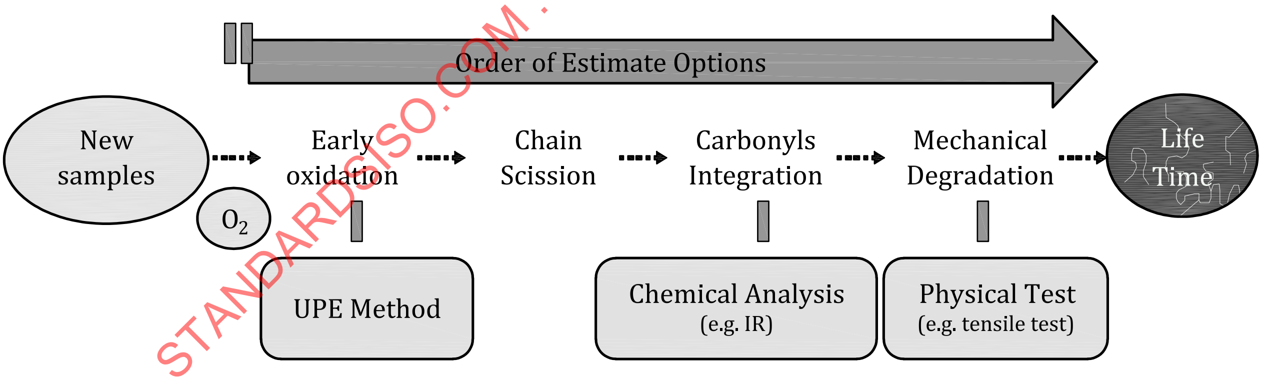


Figure A.2 — Autoxidation mechanism

A.2 Oxidation deterioration stage and evaluation method

Among the stages of deterioration in the autoxidation mechanism, each stage detected and evaluated by various measurement methods for evaluating oxidation deterioration is simplified and illustrated in Figure A.3. In the evaluation methods for the determination of structural changes, such as infrared spectrophotometer (IR) and nuclear magnetic resonance (NMR), oxidation deterioration can be first detected at the stage in which the functional groups are accumulated to some extent due to oxidation of carbonyl etc. Furthermore, the physical evaluation methods such as tensile test and impact test evaluate the second half of the process where deterioration advances until molecular weight decreases considerably. On the other hand, the UPE method demonstrates direct and highly sensitive detection of ROOH, which is an intermediate product of oxidation reaction, and therefore is capable of detecting oxidation deterioration in the very early stage.



NOTE 1 The UPE method is capable of detecting oxidative deterioration highly sensitively at the very early stage (deterioration in several hours to dozens of hours).

NOTE 2 Conventional methods (chemical analysis and physical test) are capable of detecting oxidative deterioration only after oxidation proceeds to some extent (deterioration in several hundreds of hours to several years).

Figure A.3 — Stages of oxidative deterioration

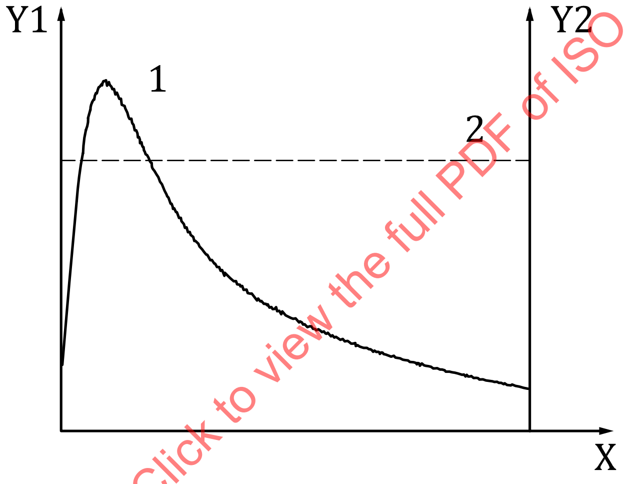
A.3 Interpretation of measuring results

Within one sequence of sensitivity check and subsequent sample measurements, a semi-quantitative comparison ("relative units") might be drawn from observed UPE to amount of oxidation products formed. Comparing different sample compounds also will mean having different UPE quantum efficiencies to be taken into account.

However, the absorption and transparency and infusibility of the sample surface to oxygen changes the reaction rate/diffusion rate ratio and the increasing conversion rate of the oxidation reaction duration will change this. The quantum efficiency of the oxidation of the components of the sample also changes with increasing conversion rate.

Already, the kind of experiment chosen determines the possible interpretation.

The simplest experimental setup, the isothermal measurement, is shown in Figure A.4 (see 8.2 b): Heating the sample to a certain temperature level under inert gas, the emission during the heat up under inert gas results from peroxides present in the sample.

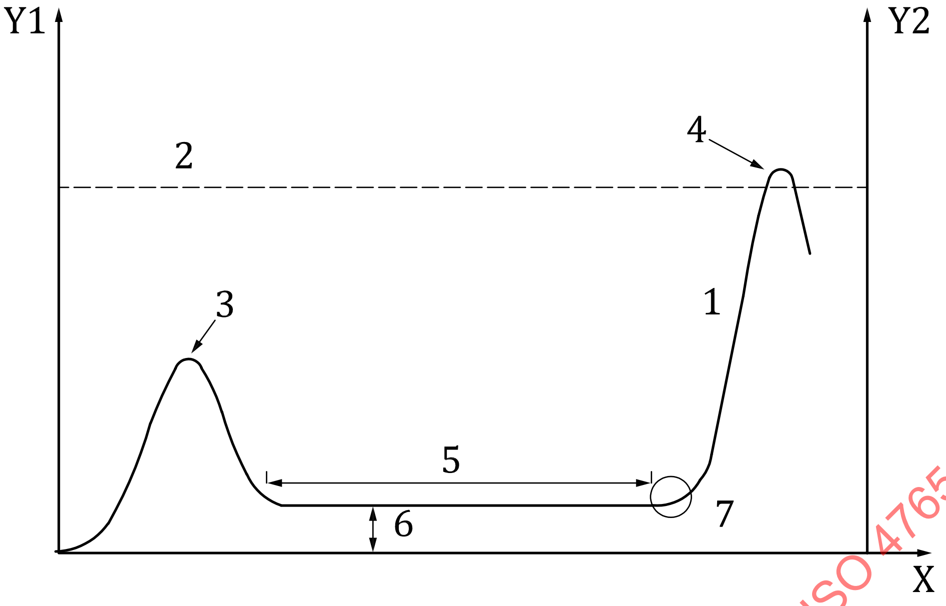


Key

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

Figure A.4 — Time course of emission intensity for isothermal measurement in inert gas atmosphere (example)

The typical UPE time course change under air or oxygen is shown in Figure A.5. The 1st peak also results from peroxides present in the sample. Typically, an induction period is observed after the 1st peak where the emission intensity keeps constant at some level depending on the sample nature such as kind of polymer, antioxidants concentration. At this stage of the initiation of the autoxidation radical chain process, concentration of radicals formed is equivalent to that deactivated. The intensity here called I_S (the steady state intensity; corresponding to the initiation rate of peroxy radical formation) and the length of this period are indicative of the stabilisation of the sample. The following evolution of UPE's rise to a maximum and subsequent levelling off reflects the rate of the oxidation reaction after the equilibrium autoxidation process before emission's rise collapses. The time of build-up of emission corresponds to the acceleration onset of the oxidation reactions composed mainly of accumulation and decomposition of hydroperoxides. It is called oxidation induction time (OIT). It first rises to a maximum as long as oxidizable species can be formed at that temperature and as long as the diffusion of oxygen into the sample can follow the reaction rate. At the UPE's maximum, the hydroperoxides decomposition rate would be close to zero due to its consumption and decrease of the materials to be oxidized.



Key

X	time
Y1	emission intensity
Y2	temperature
1	emission intensity curve
2	sample chamber temperature
3	first peak
4	second peak
5	steady state
6	steady state intensity (I_S)
7	oxidation induction time (OIT)

Figure A.5 — Typical time course change of emission intensity in oxidation accelerating atmosphere

The height of the maximum is proportional to the amount of oxidized products formed but other factors influencing the emission (UPE apparatus constant, quantum efficiency) can have changed too.

The maximum as opposed to a continuous increase of UPE may arise for a number of reasons:

- the diffusion rate cannot keep up with the oxidation rate, the so-called diffusion limited oxidation becomes dominating over reaction rate and diffusion becomes rate determining (this can be the result of a crosslinked surface or of oxidation products on the surface that are constraining the diffusion of oxygen);
- the UPE is absorbed by oxidation products on the surface or components migrating from the inside of the sample to the surface, both of which are changing the quantum efficiency;
- at the high reaction rate in the maximum the amount of oxidizable polymer at this temperature level could not be increased further.

After the maximum, the UPE levels off to a much lower, though typically not zero, level. This corresponds to the termination episode of the autoxidation reaction.

If the UPE experiment is followed by a subsequent higher temperature level under oxygen (achieved after a heating ramp under inert gas), new oxidizable species can be made available by the autoxidation reaction and the UPE will increase over the level of the termination reaction reached on the previous level.

A stepwise increasing temperature curve can be used for determining the temperature dependence of the oxidation reaction monitored with UPE. This then can be used to calculate apparent activation energies supposing an Arrhenius-like relationship.

Annex B

(informative)

Examples of time courses of UPE of thermally oxidized polypropylene (PP) for isothermal and non-isothermal measurement

B.1 Sample preparation

The samples were prepared as follows.

a) An oxidized PP plate was prepared.

b) A 10 mm^2 size of the samples was cut out into an aluminium sample dish of Ø 20 mm for non-isothermal measurement.

c) A 35 mm^2 size of the samples was cut into a stainless steel sample dish of Ø 50 mm for isothermal measurement.

B.2 Measurement procedure

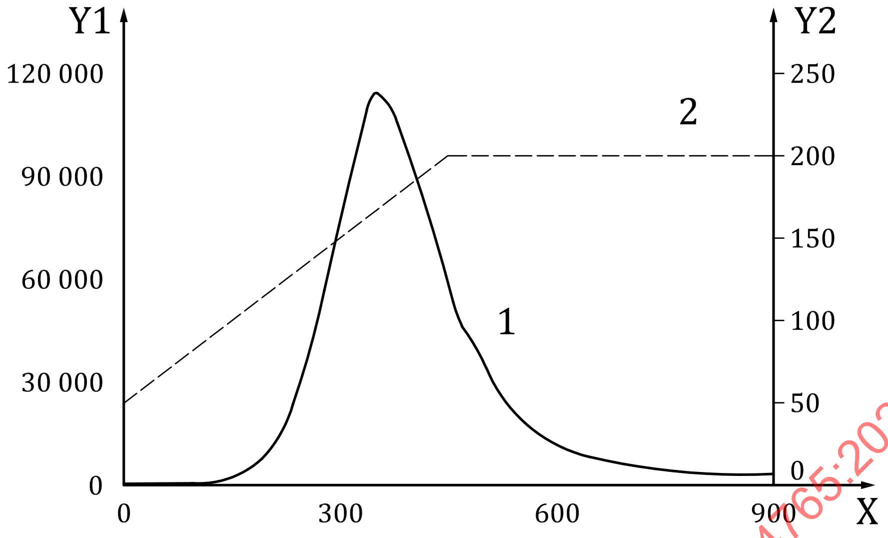
a) Non-isothermal measurement: The temperature was raised from room temperature (RT) to 200 °C under nitrogen gas flow. The specific temperature was detected at which peroxide-related reactions occur and UPE will be observed.

b) Isothermal measurement: The temperature was kept at the specific temperature determined by the results of non-isothermal measurement.

c) The atmosphere was nitrogen, and the flow rate was 50 ml/min. The gate time was 1 s, and the measurement time was 15 min and 10 min.

B.3 Measurement results

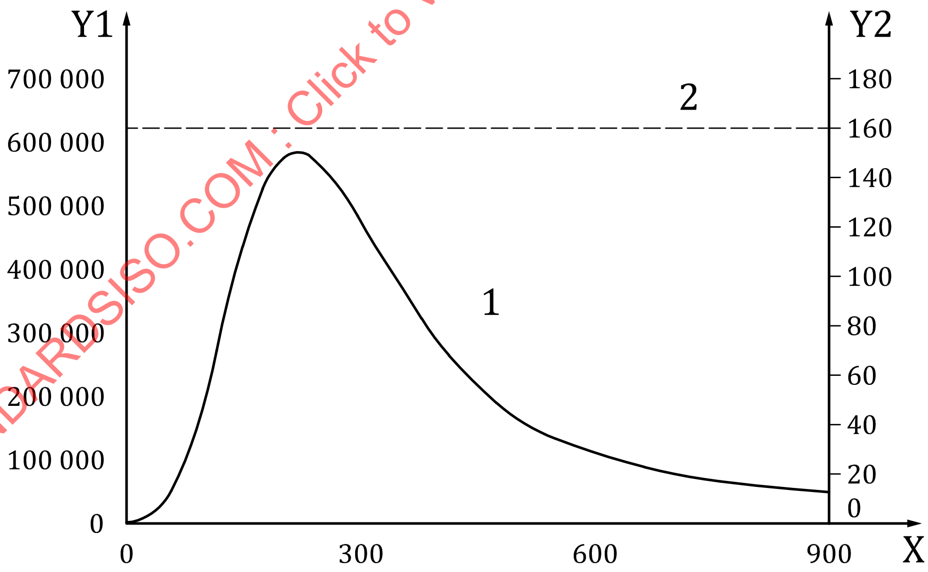
As shown in Figure B.1, UPE generally changed with passage of time at non-isothermal measurement. When the temperature reached the point at which peroxide-related reactions occur, UPE peak appears. By detecting this point, the specific temperature for isothermal measurement is determined, i.e. 160 °C in this example. The result of isothermal measurement is shown in Figure B.2.



Key

X	time in s
Y1	emission intensity in cps
Y2	temperature in °C
1	emission intensity curve
2	sample chamber temperature

Figure B.1 — Example time course of UPE of thermally oxidized PP for non-isothermal measurement



Key

X	time in s
Y1	emission intensity in cps
Y2	temperature in °C
1	emission intensity curve
2	sample chamber temperature

Figure B.2 — Example time course of UPE of thermally oxidized PP for isothermal measurement

Annex C

(informative)

Example of measurements of oxidation deterioration degree of thermally oxidized polyethylene (PE)

C.1 Sample preparation

The samples were prepared as follows.

a) Three sheets with a dimension of 3 cm^2 and a thickness of 1 mm by heat pressing from pellets of linear low-density polyethylene (LLDPE) were prepared.

b) These sheets were put into an oven (air atmosphere) at a temperature of 200 °C, and were held for 1 h, 2 h and 3 h, respectively.

C.2 Measurement procedure

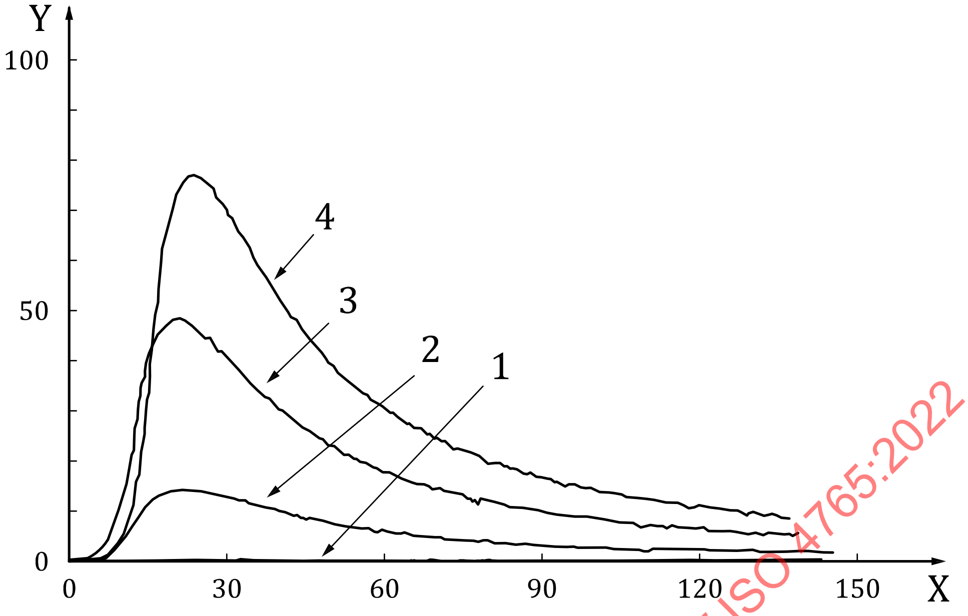
a) The temperature was kept at a constant temperature of 90 °C.

b) The atmosphere was argon, and the flow rate was 50 ml/min. The gate time was 1 s, and the measurement time was 150 min.

C.3 Measurement results

As shown in Figure C.1, the hot-press mold sample without heating in the oven does not show any UPE in argon at 90 °C. On the contrary, the sample heated in air at 200 °C generates remarkable light emission, and the emission intensity (peak intensity and integrated intensity) increases with an increase in heating time. This result indicates that the heating in air accelerates oxidation of LLDPE and produces peroxide in the sample, and that the concentration of the peroxide becomes higher with the heating time.

The UPE measurement of the sample in inert gas makes it possible to compare the degree of oxidative deterioration relatively among samples of different aging history.



Key

X time in min

Y emission intensity in 10^2 cps

1 0 h

2 1 h

3 2 h

4 3 h

Figure C.1 — Example of UPE measurements of thermally oxidized polyethylene

Annex D
(informative)

Example evaluation of oxidation induction time (OIT)

D.1 Sample preparation

The samples were prepared as follows.

a) Commercial PP pellet without antioxidant, and PP pellets containing antioxidant of 0,5 wt% and 1,0 wt%, respectively were prepared. With these materials, samples of injection molded PP plates (7 mm in diameter × 1 mm in thickness) were prepared.

b) The fixed quantity of the samples was weighed and set into an aluminium container of Ø 20 mm or Ø 30 mm.

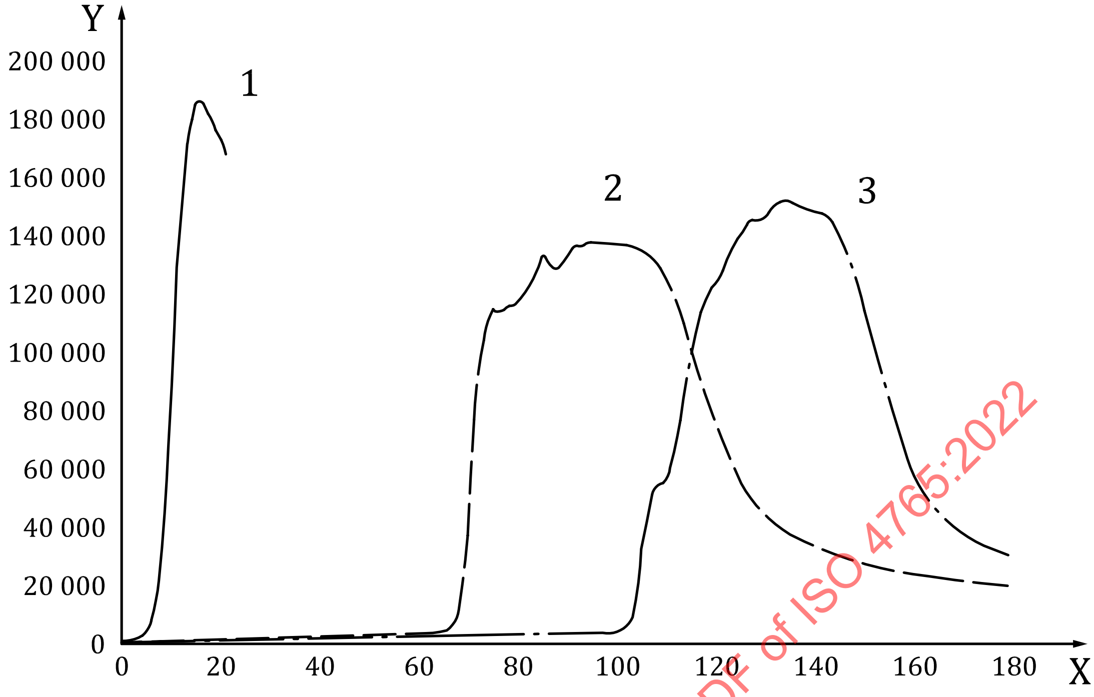
D.2 Measurement procedure

a) The temperature was kept at a constant temperature at 200 °C.

b) The atmosphere was oxygen, and the flow rate was 50 ml/min. The gate time was 1 s, and the measurement time was 7 h.

D.3 Measurement results

The time course of UPE intensity of PP pellet with different amount of antioxidants is shown in Figure D.1.



Key

X time in min

Y emission intensity in cps

1 PP without antioxidant

2 PP with 0,5 % antioxidant

3 PP with 1,0 % antioxidant

Figure D.1 — Example of change in oxidation induction time (OIT) of PP pellet with different concentration of antioxidants

OIT increases in correlation with the concentration of stabilizers added to PP, which indicates the oxidation retardation effect of stabilizers. In this manner, OIT can be used as an index of ease of oxidation of the sample, effect of stabilizers or prediction of the end of life caused by heat ageing.

The OIT evaluation requires an evaluation period of several hours to several days.