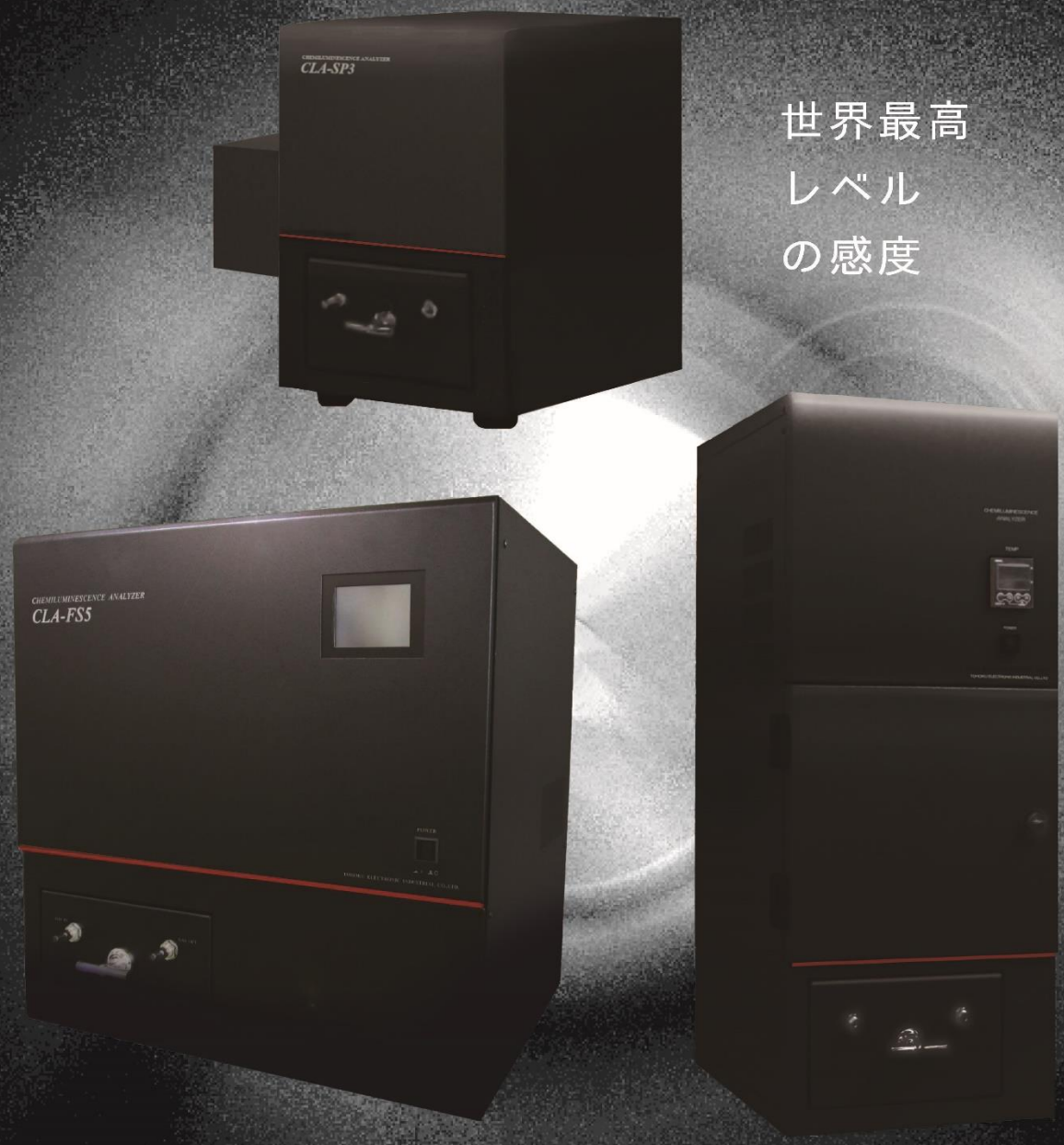
World-beating
sensitivity

世界最高
レベル
の感度



CHEMILUMINESCENCE ANALYZER

Ultraweak luminescence detector systems

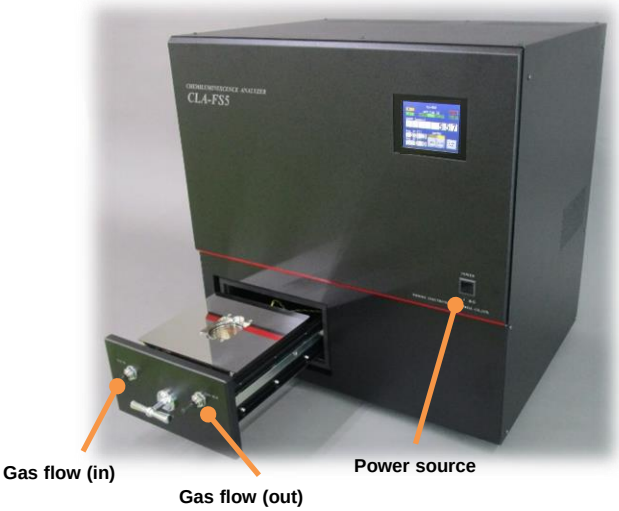
TOHOKU 東北電子産業株式会社

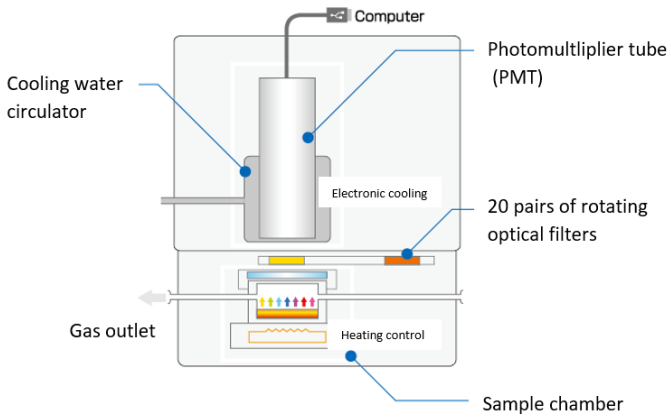
Tohoku Electronic Industrial Co., Ltd.

Overview of Chemiluminescence Analyzers

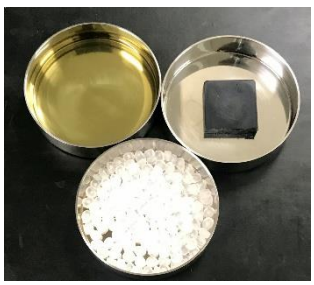
CLA-FS5

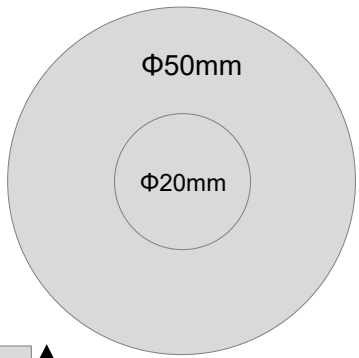
Using a photomultiplier tube (PMT), this is our most sensitive luminescence measurement device.





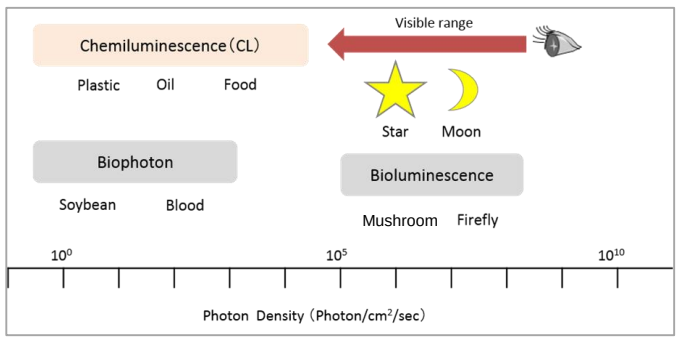
Typical samples





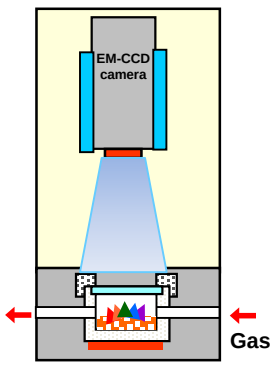
Solids, liquids and powders can also be measured, as long as they fit into a dish with a diameter of 50mm or 20mm.

Luminescence detection range



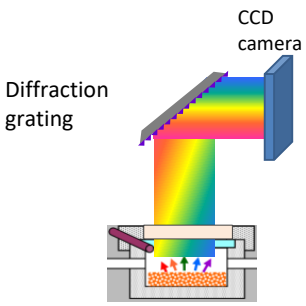
CLA-IMG

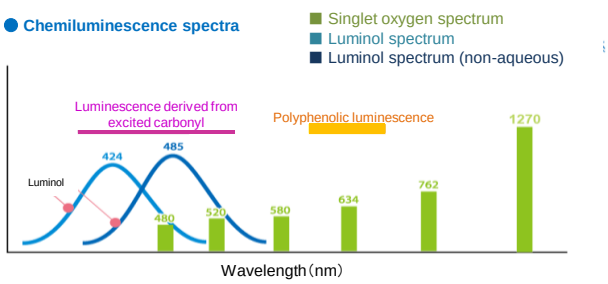
A built-in ultrasensitive CCD camera enables this device to identify oxidised areas and perform measurements on multiple samples simultaneously.



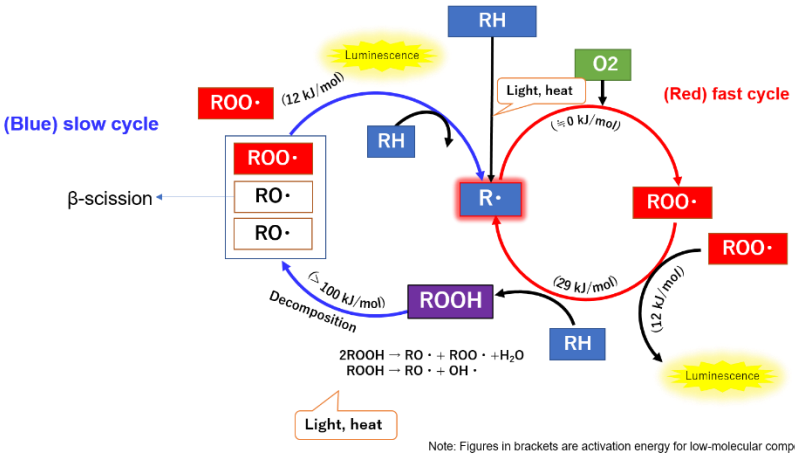
CLA-SP3

This is an instantaneous photometric weak-emission spectrum measurement device combining a high-sensitivity CCD camera with a bright spectrometer.

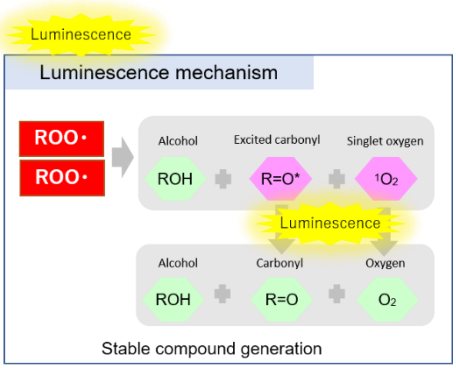




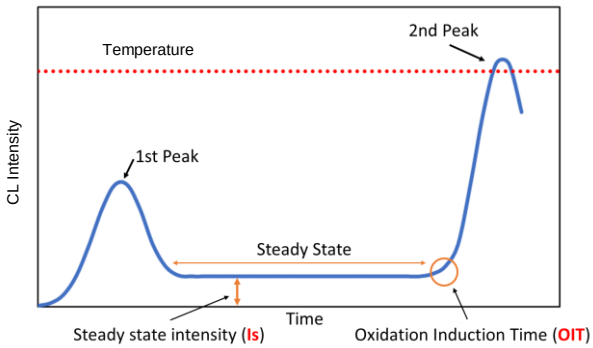
Auto-oxidation mechanism and luminescence phenomena



Note: Figures in brackets are activation energy for low-molecular compounds



Data analysis method during heating measurement

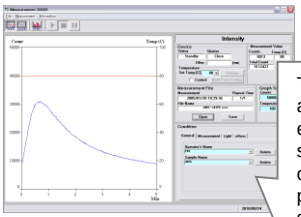


The graph on the left shows typical CL behaviour during heating measurement. As the sample is heated, the peroxide decomposes, and CL from the excited carbonyl increases, resulting in a peak (the first peak). This corresponds to the amount of peroxide at that point.
The oxidation reaction is then accelerated by heating in air or oxygen, and eventually the CL reaches a steady state. The intensity at this time is termed the steady-state luminescence intensity (**Is**). In the sample to which stabiliser has been added, the stabiliser is consumed, the steady state of the oxidation reaction is disrupted, and the amount of radicals in the sample increases, resulting in the appearance of significantly higher luminescence (the second peak). This point is called the oxidation induction time (**OIT**). The OIT can be used to evaluate the oxidative stability of the sample. Also, since **Is** is the steady state of radical extinction and formation within the sample, it represents the rate of radical generation, and this value can also be used to evaluate the oxidative stability of the sample.

Measurement Modes

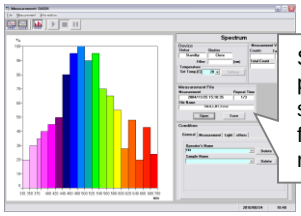
CLA-FS5

CL Intensity measurement



The amount of luminescence at all wavelengths is measured for each exposure time setting (0.1 sec, 1 sec, 10 sec). The degree of oxidation is determined by parameters such as the height, slope, time and total area of the luminescence peak.

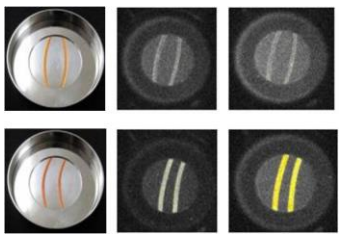
CL Spectrum measurement

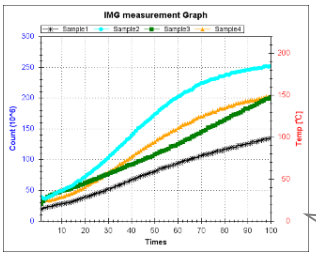


Spectrum measurement is performed while the spectral filter (high-pass filter) built into the device rotates automatically.

CLA-IMG

CL Image measurement

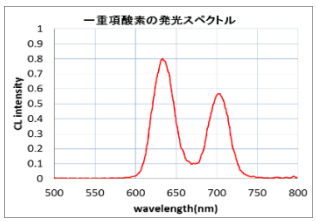




Numerical values can be displayed within the selected range of the image.

CLA-SP3

CL Spectrum measurement

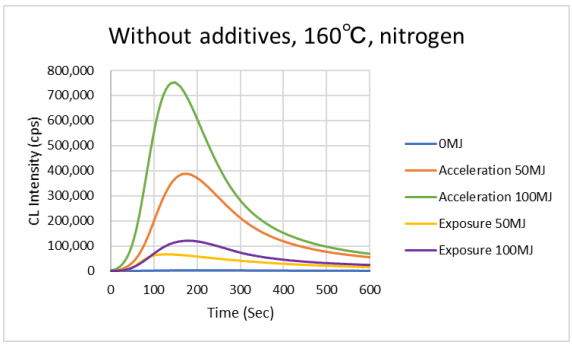


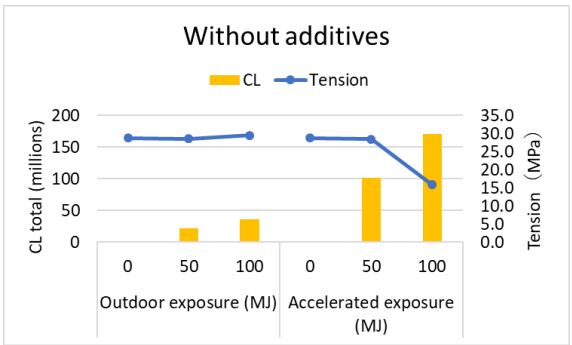
Instantaneous spectrum measurement can be performed with high resolution of 1nm or less.

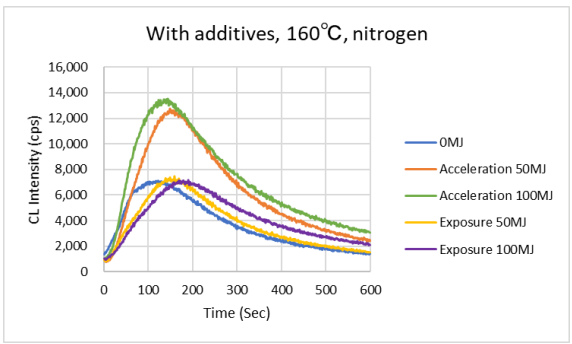
Measurement Examples (Polymers)

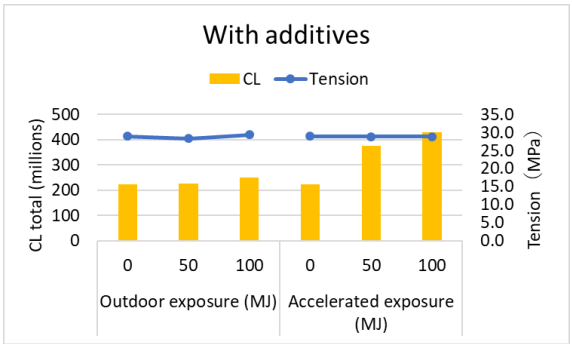
Weather resistance evaluation

Samples	Polypropylene subjected to exposure testing and acceleration testing, with and without additives (HALS, UVA)
Exposure conditions	50MJ (approximately 2 months), 100MJ (approximately 4 months), JIS K 7219, exposure tests performed in Osaka
Acceleration conditions	50MJ (equivalent to 177 hours), 100MJ (equivalent to 353 hours), JIS K 7350-4, Sunshine Weather Meter
Measurement conditions	160℃, nitrogen, CLA-FS4







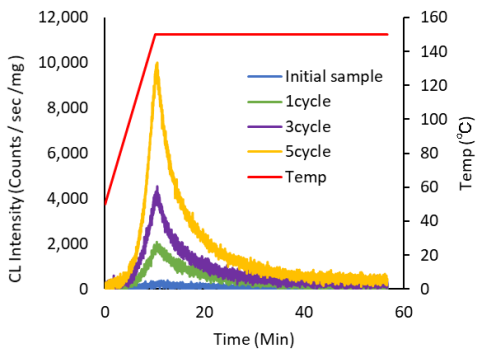


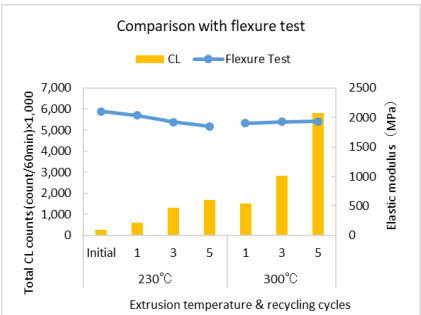
The “with additives” exposure-tested samples showed only a slight difference, but the acceleration-tested samples showed an increase in the amount of luminescence as they degraded, indicating a small difference in oxidative degradation at the very beginning.
In the tensile test, a difference in the value was first seen in the “without additives” acceleration-tested sample oxidised at 100MJ.

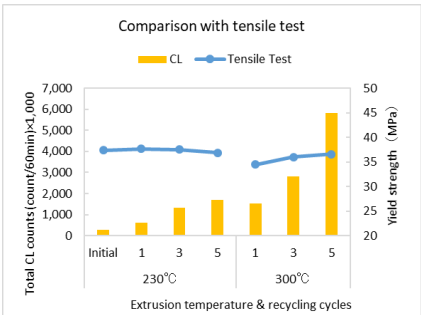
Samples were supplied by the Japan Chemical Innovation and Inspection Institute (JCII), along with acceleration test, exposure test and physical property test support.

Evaluation of recycled materials

Samples	Polypropylene (PP) pellets manufactured at different extrusion temperatures and cycle counts
Extrusion conditions	Temperatures: 230°C, 300°C; cycle counts: 0, 1, 3, 5
Measurement conditions	150°C, nitrogen, CLA-FS4







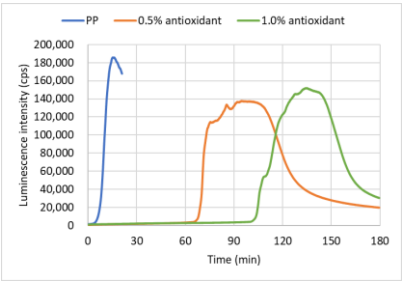
The higher the recycling cycle count, the higher the amount of luminescence shown; slight oxidation due to recycling could be detected.
In the physical property tests (the flexure test and tensile test), hardly any difference was observed.

Measurement Examples (Polymers)

Evaluation of oxidation induction time (OIT)

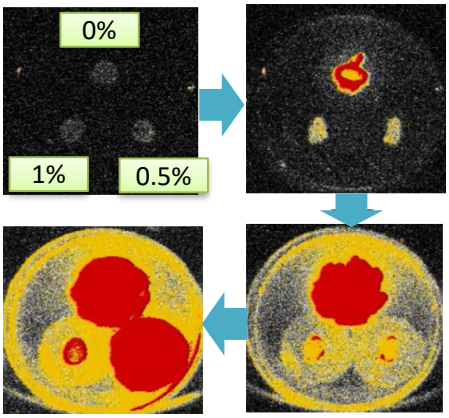
Samples	Polypropylene (PP) pellets with different concentrations of additive (Irganox 1010)
Measurement conditions	CLA-FS4: 200°C, oxygen; CLA-IMG: 200°C, oxygen

OIT data measured using CLA-FS4



Luminescence image measurement

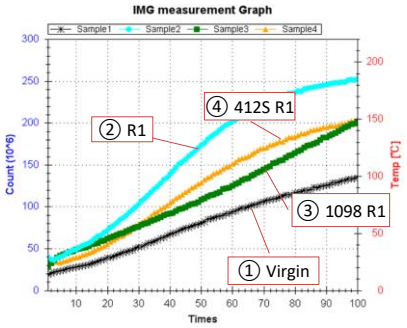
OIT image measured using CLA-IMG



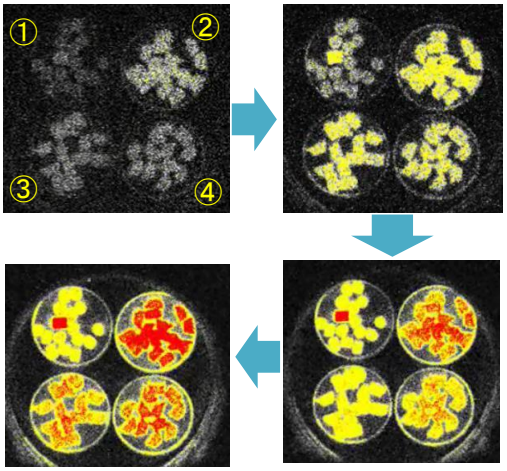
Amount of luminescence

Large — Small

Samples	Polyamide pellets ① Virgin: Unoxidised, without additive ② R1: Recycled, without additive ③ 1098_R1: Irgafos 1098, recycled ④ 412S_R1: AO-412S, recycled
Measurement conditions	CLA-IMG: 200°C, oxygen

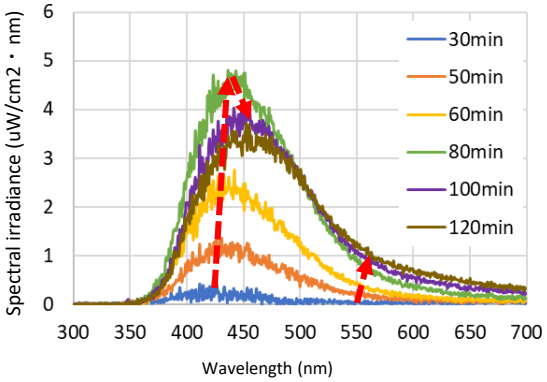


Luminescence image measurement



Luminescence spectrum during thermal oxidation

Samples	Polypropylene (PP) pellets
Measurement conditions	200°C, oxygen, CLA-SP3

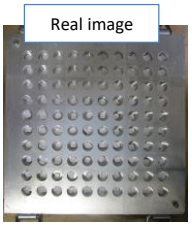


With oxidation, a long wavelength shift was observed in the peak position in the 400nm range, and an increase in intensity was observed in the long wavelength region of 550nm and above.

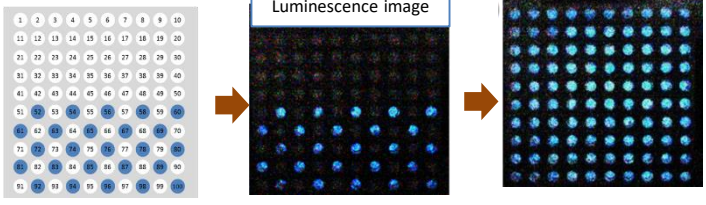
Simultaneous measurement of 100 samples

Samples	Polypropylene (PP) pellets
Measurement conditions	200°C, oxygen, CLA-100

Real image

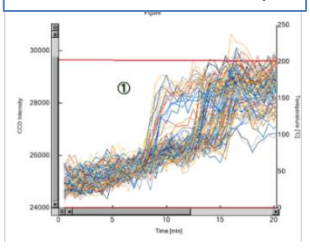


●: PP; ○: PP + antioxidant



OIT measurement was carried out simultaneously on 100 samples. In the PP without the antioxidant, the OIT was shorter, and the OIT time course could be detected with good reproducibility, without being affected by adjacent samples.

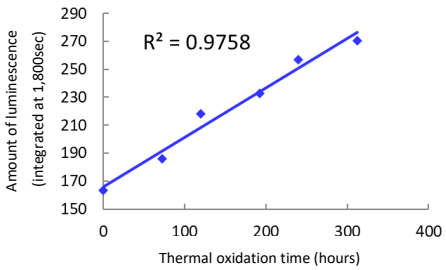
CL time course for each sample

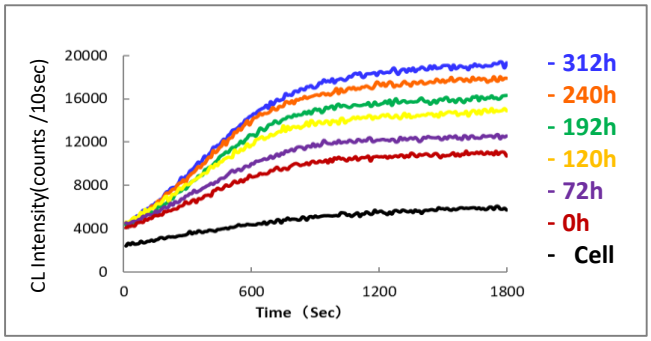


Measurement Examples (Polymers)

Evaluation of thermal oxidation of rubber

Samples	Natural rubber with carbon black
Heat processing	100°C, 72 to 312 hours
Measurement conditions	160°C, oxygen, CLA-FS3



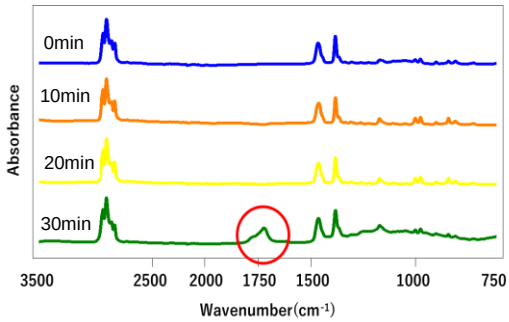


The longer the thermal oxidation time, the higher the amount of luminescence (see graph above); the integrated amount of luminescence at 1,800sec showed a high positive correlation with the thermal oxidation time (see graph on left).

Comparison with infrared (IR) absorption measurement

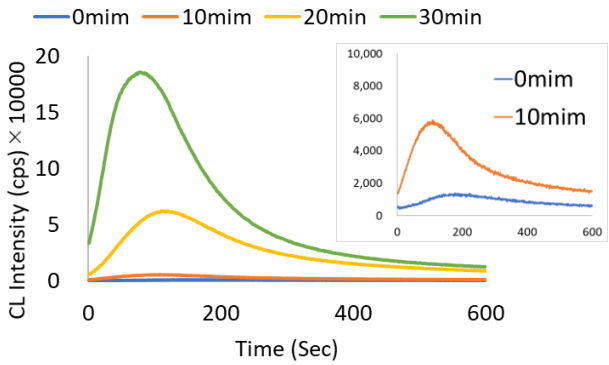
Samples	Polypropylene powder
Degradation conditions	Heating at 160°C for 10 to 30 minutes
Measurement conditions	160°C, nitrogen, CLA-FS4

FT-IR



Magnified view

CL

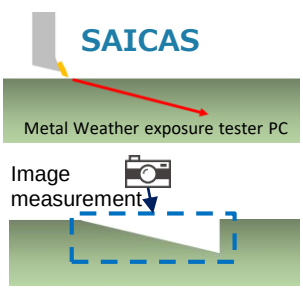


With the infrared absorption measurement method, a peak derived from the carbonyl group was visible in the sample after 30 minutes of heating (see graph on left), but with the CL method, an increase in luminescence was observed after 10 minutes of heating.

Samples supplied by: Sumitomo Chemical Co., Ltd.

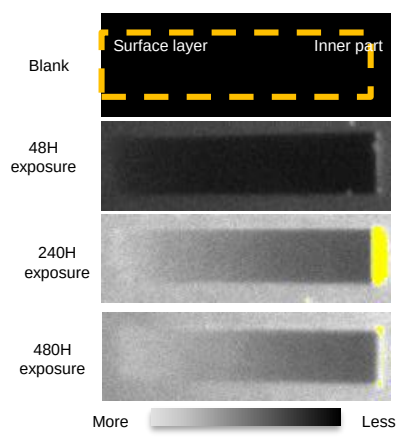
Magnified image measurement using CCD camera

Samples	Polycarbonate, thickness: 5mm
Degradation conditions	Metal Weather exposure tester
Measurement conditions	Using a SAICAS system, oblique cutting was performed to a depth of 25μm, and CL imaging measurement was performed on the cut surface. Laser irradiation (375nm, 10mW), CLA-IMG



The more luminous (white) the sample, the more the oxidative degradation has progressed. Gradation was seen from the surface layer to the inner part.

CL image from top of sample

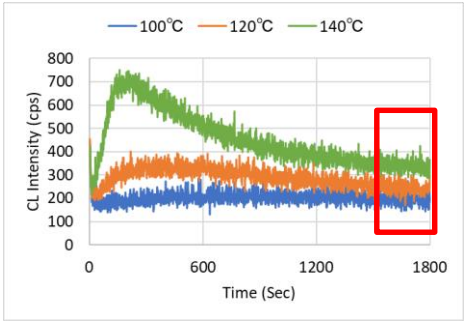


Slides supplied by: Daipla Wintes Co., Ltd.
Data supplied by: C. I. Takiron Corporation

Measurement Examples (Polymers)

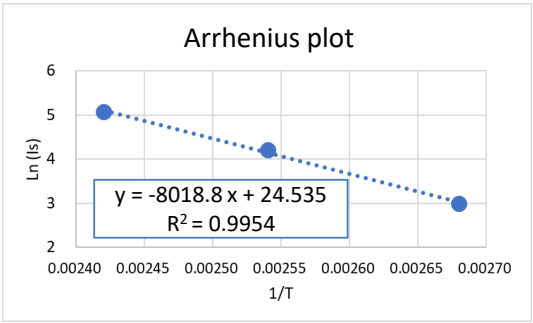
Calculation of activation energy

Samples	Polypropylene (PP) pellets
Measurement conditions	100°C, 120℃, 160°C, oxygen, CLA-FS4



	100°C	120°C	140°C
1/T	0.0026	0.0025	0.0024
Is	191.62	239.12	331.73
Ln (Is)	3.00	4.21	5.08

1. Oxidation of the samples was accelerated under oxygen flow at each temperature condition, and the average value was calculated for the value (Is) where luminescence stabilized after the first peak.
2. Ea (activation energy) was determined from the slope of the equation of the approximation curve, with LN (Is) plotted as the vertical axis, and 1/T (absolute temperature) as the horizontal axis.



Slope（-8018.8) x gas constant ＝ **66.7kJ/mol**

Ea can be calculated by measuring CL under multiple temperature conditions.

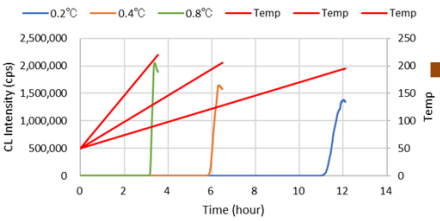
Samples supplied by: Sumitomo Chemical Co., Ltd.

Lifespan prediction

Samples	Polypropylene (PP) pellets
Measurement conditions	50 to 250°C, oxygen 0.2°C/min, 0.4°C/min, 0.8°C/min, CLA-FS4
Analysis software	AKTS - Thermokinetics

Reaction kinetics analysis program
Friedman differential equivalent method
System improving on the (Ozawa) integral equivalent method

①



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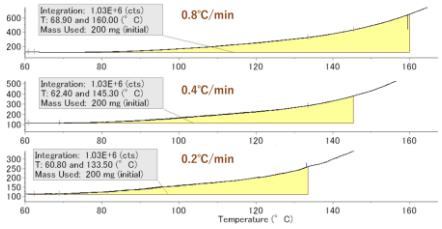

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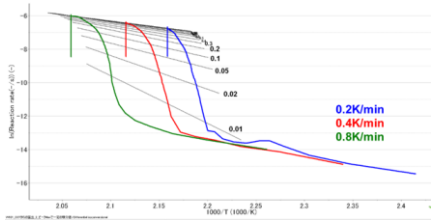

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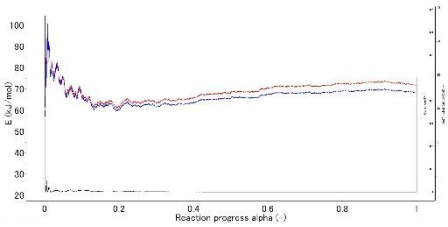

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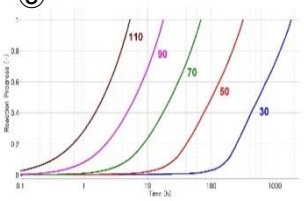

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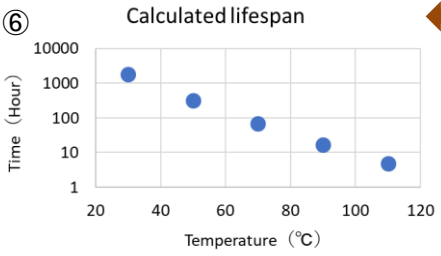


1. CL data
2. Time-course graph of integrated value over time for amount of luminescence
   Reaction progress is represented as an integrated value over time. The integrated amount of luminescence at the point at which the temperature reached 160℃ (melting point or lower) from the start of measurement at 0.8℃/min was taken to be the reaction end point. The reaction progress at this point was taken to be 1, and regarded as the lifespan.
3. The Ln (dα/dt) for α (reaction progress) was determined from a graph of the relationship between the reciprocal of each temperature and the logarithm of the reaction speed. This slope is the Ea (activation energy); the Ea for each α can be determined.
4. Activation energy
5. Lifespan prediction results at constant temperatures (30℃, 50℃, 70℃, 90℃, 110℃) (vertical axis: reaction progress; horizontal axis: time)
6. Lifespan prediction (bar graph)

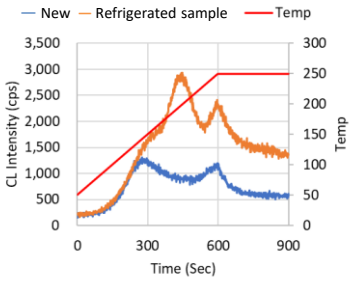
This suggests that lifespan can be predicted by means of CL measurement under multiple temperature-elevation measurements, without acceleration testing.

Samples supplied by: Sumitomo Chemical Co., Ltd.;
Analysis support: Palmetrics Corporation

Measurement Examples (Food)

Measurement of rapeseed oil (1)

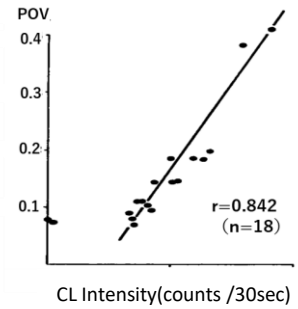
Samples	Rapeseed oil New, refrigerated for 2 years
Measurement conditions	50 to 250℃, nitrogen, CLA-FS4



The amount of luminescence was higher in the sample refrigerated for 2 years than in the new sample, and multiple luminescent components were observed by means of temperature-elevation measurement.

Measurement of rapeseed oil (2)

Samples	5g rapeseed oil
Measurement conditions	150℃, nitrogen, CLA-ID

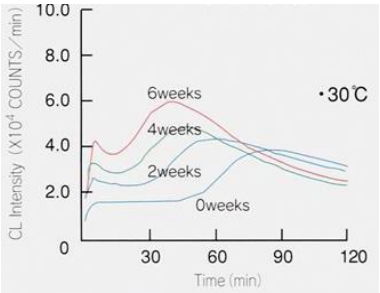


The CL integrated value and the POV value showed a high correlation.

R. Ushuki, Nippon Shokuhin Kogyo Gakkaishi 32 (1), 74 (1985)

Luminescence of beer

Samples	1.2ml beer
Degradation conditions	Stored at 30℃ for up to 6 weeks
Measurement conditions	60℃, CLA-ID



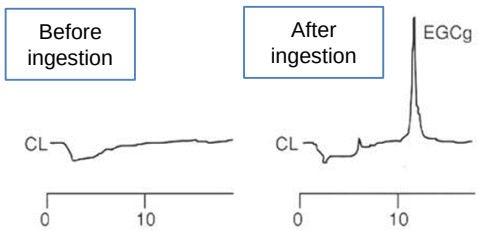
The longer the storage period, the more the CL increased.

H. Kaneda et.al., Journal of Food Science, 55 (5), 1361-1364, 1990

Measurement of catechins in human blood

Samples	Catechin extract in plasma
Mobile phase	Methanol-water (2:8, v/v, containing 0.1% phosphoric acid), 1.0ml/min
Reagents	① 8.0M acetaldehyde in 50mM phosphate buffer at pH 7.4, containing HRP 108mg/L, 3.0ml/min ② 8.8M H2O2, 1.0ml/min
Measurement conditions	CLA-FL, HPLC system

Detection of EGCg luminescence in human plasma, before and after ingestion of EGCg



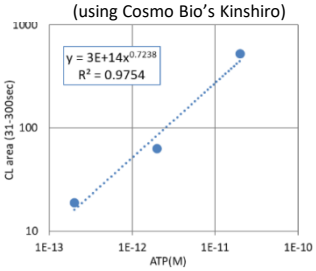
Nakagawa, K. and Miyazawa, T.: Analytical Biochemistry, 248, 41-49, 1997

Luminescence peaks of epigallocatechin gallate (EGCg) were detected in plasma 60 minutes after ingesting an EGCg capsule.

Measurement of ATP

Samples	ATP reagent manufactured by Cosmo Bio
Measurement conditions	Room temperature, air, CLA-IDsp

ATP measurement by means of L-L reaction (using Cosmo Bio's Kinshiro)

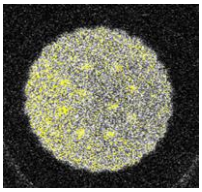


Luminescence up to about 1x10^{-13}M showed good linearity, with a correlation coefficient of 0.97.

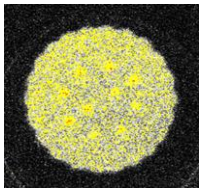
Luminescence of cookies

Samples	Cookies (deep-fried confectionery)
Degradation conditions	254nm, irradiation for 0 to 1 hour
Measurement conditions	100℃, nitrogen, CLA-ID

Unirradiated



Irradiated for 1 hour

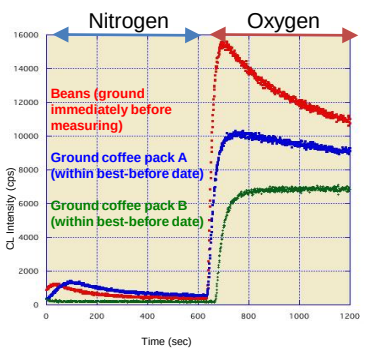


The amount of luminescence increased after 1 hour of light irradiation.

Samples supplied by: Kochi Prefecture Paper Technology Center

Measurement of coffee

Samples	Columbian medium-roasted beans
Measurement conditions	80℃ nitrogen → oxygen, CLA-FS4



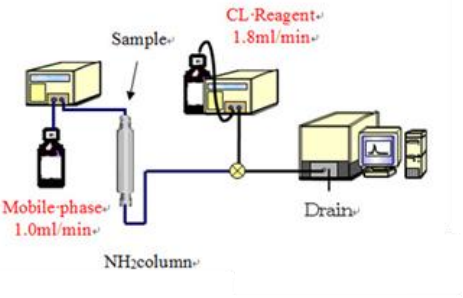
Immediately after grinding, the amount of luminescence was higher and the fragrance and flavour were also better. The amount of luminescence decreased with storage time.

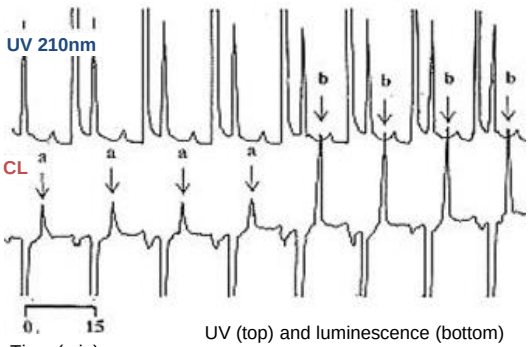
Samples supplied by: La Coet

Measurement Examples (Biochemical)

Measurement of phospholipid hydroperoxides (PCOOH) in blood

Samples	Catechin extract in plasma
Mobile phase	2-propanol-methanol-water (135:45:20, v/v/v)
Reagents	10mg of cytochrome c and 2mg of luminol dissolved in 1L of 50mM borate buffer solution
Sample	Photo-oxide of L-α-phosphatidylcholine, β-oleoyl-γ-palmitoyl (C18:1, [cis] -9/C16:0, SIGMA)
Measurement conditions	CLA-FL HPLC system (column: SIL-NH2)





Time (min)

UV (top) and luminescence (bottom) chromatograms for PCOOH

R-OOH + cytochrome ***c*** → reactive oxygen
reactive oxygen + luminol oxidized luminol
oxidized luminol → *hv*

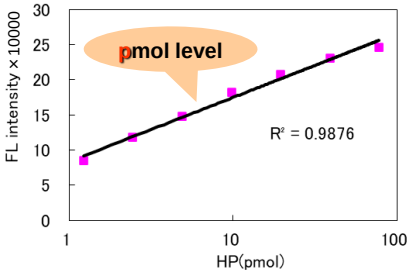
CL-HPLC chromatograms were obtained for normal subjects a and b. The amount of PCOOH for subject a (several hundred femtomoles) was less than for subject b (several picomoles), and could be detected with good reproducibility. Lipid peroxides in human blood are an indicator of oxidative stress in the body.

Guidance provided by: Professor Teruo Miyazawa, Tohoku University Graduate School of Agriculture

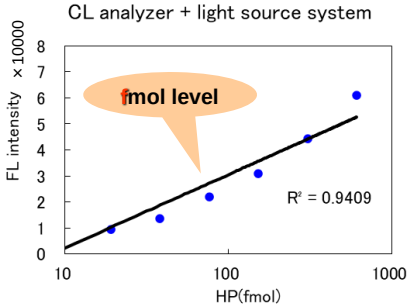
Ultra-sensitive fluorescence measurement

Samples	Haematoporphyrin
Measurement conditions	LD 405nm + HP 600nm Room temperature, air, CLA-FS4

Conventional Fluorescence Method



CL analyzer + light source system



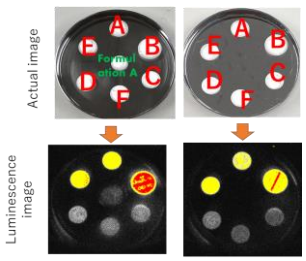
In contrast to the method using a general fluorescence spectrophotometer, this method enabled a calibration curve to be obtained to about 20fmol.

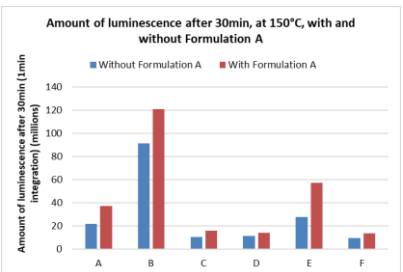
Measurement of tablets

Samples	Tablets of the same kind
Degradation conditions	Experiment 1: All new tablets Experiment 2: photodegraded tablets (1 week under indoor diffused light, 2 weeks under 4000Lux)
Measurement conditions	Experiment 1: 150℃, oxygen, exposure for 1 min, sensitivity: 255, CLA-IMG Experiment 2: 150℃, nitrogen, exposure for 1 min, sensitivity: 255, CLA-IMG

With and without a formulation of different constituents (Formulation A) placed in the middle

Experiment 1

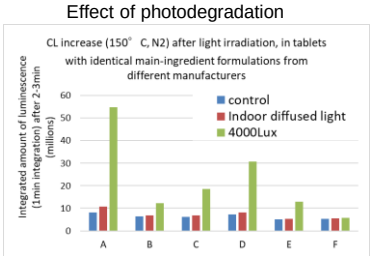




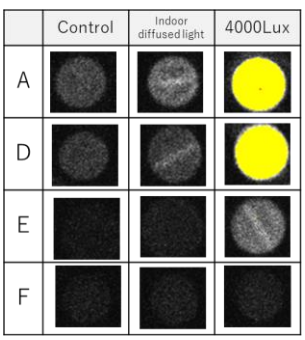
The amount of luminescence was higher, and oxidation was more prone to occur, when Formulation A was present.

Experiment 2

Effect of photodegradation



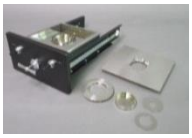
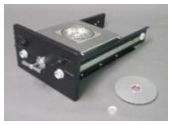
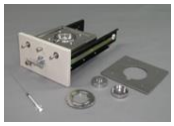
Although the tablets had the same main constituents, a difference was seen in the rate of increase.



Specifications

Product name	CLA-FS5	CLA-ID5
Photograph		
Detection method	Single photon counting method using a photomultiplier tube	
Detection wavelength	300nm to 650nm (centre wavelength: 420nm)	
Cooling method	Primary cooling: Peltier element; Secondary cooling: water cooling	
Measurement items	① Luminescence intensity (counts per second) ② Luminescence spectrum (380nm to 660nm/20nm resolution)	Luminescence intensity (counts per second)
Minimum measurement time (Gate time)	0.1 sec, 1 sec, 10 sec	
Spectral filters	15, built-in (380nm to 660nm: every 20nm)	None
Touch panel display items	① Amount of luminescence, ② Sample chamber temperature, ③ Sample chamber temperature setting, ④ Status, ⑤ Gate time, ⑥ Alarm, ⑦ Detail, ⑧ Sample chamber status (open/closed), ⑨ Shutter status (open/closed)	
Communication functionality	1 USB port (used by dedicated software)	
Dimensions, weight	523.5mm (W) x 411.5mm (D) x 547mm (H) Approx. 60kg	310mm (W) x 420mm (D) x 524mm (H) Approx. 35kg

Sample Chamber Specifications

Product, model	Sample Chamber (Heating Type to 220°C) CLS-ST5	Sample Chamber (Non-isothermal Type) CLS-SH2	Sample Chamber (Mixing Type) CLS-MX5	Sample Chamber (Flow Type) CLS-FL2
Maximum sample size	50mm diameter x 10mm (H)	20mm diameter x 5mm (H)	50mm diameter x 10mm (H)	Flow tube bore: 0.5mm
Heating temperature	Room temperature to 220℃	Room temperature to 350℃	Room temperature to 100℃	Room temperature to 50℃
Functionality included	Atmosphere replacement	Non-isothermal functionality Atmosphere replacement	Atmosphere replacement Sample agitation Reagent injection	2 injection ports 1 drainage port
Dimensions, weight	 221mm (W) × 357mm (D) × 121mm (H) Approx. 4kg	 221mm (W) × 357mm (D) × 121mm (H) Approx. 4kg	 221mm (W) × 357mm (D) × 121mm (H) Approx. 4kg	 221mm (W) × 357mm (D) × 121mm (H) Approx. 2kg

Specifications

Product name	CLA-IMG4	CLA-SP3
Photograph		
Detection method	Back-illuminated frame-transfer CCD camera	
Detection wavelength	400 to 800nm (centre wavelength: 600nm)	
Cooling method	Air cooling	
Number of effective pixels	1024 x 1024	1600 x 200
Resolution	Vacuum resolution: approx. 150μm × 150μm (Option: approx. 10μm)	Wavelength resolution: 1nm
Measurement items	Luminescence image Luminescence intensity (within image selection range)	Luminescence spectrum measurement
Exposure time	30ms to 120min	0.01 to 10,000sec
Lens	25mm, F0.95 (C mount)	Incidence slit width: 0.1/0.5/1.0mm
Built-in shutter	Built-in mechanical shutter	None
Communication functionality	IEEE1394b	USB
Dimensions, weight	310mm (W) x 446mm (D) x 775mm (H) Approx. 30kg	310mm (W) x 420mm (D) x 524mm (H) Approx. 35kg

Sample Chamber Specifications

Product, model	**Sample Chamber (Laser-induced Fluorescence Type) CLS-LA1**
Maximum sample size	50mm diameter x 10mm (H)
Heating temperature	Room temperature to 100℃
Laser light-source wavelength	375nm or 405nm
Laser output and stability	0.1 to 20mW At 5 to 20mW: ±1% At 0.1 to 5mW: ±5%
Dimensions, weight	 221mm (W) × 357mm (D) × 121mm (H) Approx. 4kg

Accreditations and awards

2006: Certified by the Ministry of Economy, Trade and Industry (METI) of the Government of Japan as one of Japan's 300 Most Vibrant Monozukuri (Manufacturing) Small and Medium Enterprises

2009: Received Miyagi Sugure Mono (“Miyagi outstanding product”) accreditation under a promotional project spearheaded by Miyagi Prefecture and other bodies

2012: Received the Tohoku Bureau of Economy, Trade, and Industry Director-General's Award, one of the Monozukuri Nippon Grand Awards

2014: Received the First Technology Advancement Award conferred by the Japan Society of Polymer Processing

2017: Certified by METI as a Company Driving Regional Growth

2019: Certified by the Kawasaki Monozukuri (Manufacturing) Brand Promotion Council as a Kawasaki Monodukuri Brand

みやぎ 優れMONO Miyagi Sugure Mono

地域未来牽引企業

知と技で世界に羽ばたく 川崎ものづくりブランド

2018: Chemiluminescence methods named in a newly-published Japanese Industrial Standard (JIS)

K 7351

“Sensitive Measurement Method of Peroxide In Plastics By Detecting Ultra-Weak Photon Emission”

http://www.tei-c.com

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