

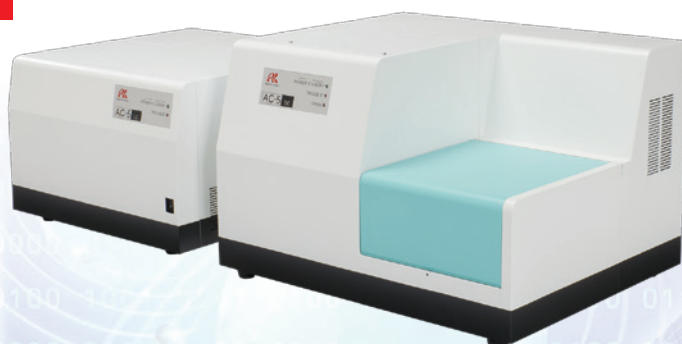
Atmospheric Photoemission Yield Spectrometers

–AC Series–

Photoemission Yield Spectroscopy in Air (PYSA)

General Catalog

Model : AC-5



A new approach to advanced technology development

–For easy measurement of work function and ionization potential–



Model : AC-2



Model : AC-3

1991: Ichimura Industry Award
2006: ADY Excellence Award
2006: Orgatechno Award
(Manufacturing & Equipment Category)
2015: Heritage of Analytical and Scientific
Instruments Certification

RIKEN KEIKI Co.,Ltd.

Allows Easy Measurement of Work Function and Ionization Potential— Accelerating **New Material Development and Evaluations**

Developed by Dr. Masayuki Uda at Riken, the Atmospheric Photoemission Yield Spectrometer (Photoemission Yield Spectroscopy in Air [PYSA]) is a kind of photoelectron spectrometry which is capable of measuring work function and ionization potential in open air. It can count the number of photoelectrons by using the open counter. It was the world's first analyzer introduced as the AC Series by Riken Keiki, and the manufacture and sale started in 1986.

In the more than 30 years since its launch, it has contributed to the development of new materials, including nanocarbon materials and organic electroluminescent displays (ELDs), and advanced research and development on evaluating materials for silicon/hard disks and the like. Nowadays, it's also used in research and development on state-of-the-art technologies in fields like new energy (for example, solar panels and fuel cells) and the food industry.

This catalog describes the features and principle of the AC Series in easy-to-understand terms, together with the features, specifications, and applications of the Riken Keiki AC Series products.

*The "AC" of the AC Series refers to "air" and "counter" (counting electrons in the air). They are now referred to as open counters after it was subsequently determined that measurement is possible in gases other than the air.

See pp. 6–8 for primary applications.



Organic electroluminescent displays

Hard disks



Solar panels



Food (beverages)



Model : AC-5

⇒p.10



Latest model with new detector

- Incorporates new detector for extended dynamic range in electron counting.
- Supports large samples up to 180 × 180 mm. (AC-2 supports sizes up to 50 × 50 mm.)
- Sample changer automates measurement.
- Allows high-intensity light measurement using Xe (xenon) lamp.

Model : AC-3

⇒p.11

Model supporting high-energy measurement

- Capable of measuring high energy of up to 7.0 eV in open air.
- Ideally suitable for measuring organic materials and thin films with high work function and ionization potential.



Model : AC-2

⇒p.11



Model widely used worldwide

- The AC-2 model is intended for use in academia.

Why Is the **AC Series** So Widely Chosen by Researchers?

- A single measurement takes approximately **five minutes**.
- Easy operation with dedicated software
 - Enabling rapid measurement of large volumes of samples

Extremely fast measurement from start to finish, with a single measurement taking approximately five minutes. The Riken Keiki AC Series also uses dedicated software that makes operation easy for anyone. Work function and ionization potential measurements previously required specialist knowledge; now, these can be measured within a short time by anyone, helping to speed up development.



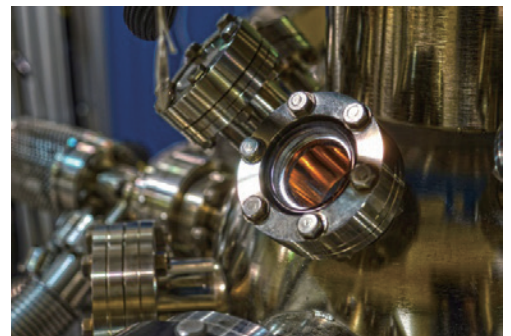
- The AC Series measure samples in open air
 - Providing results corresponding to actual conditions (Powders and liquids can also be measured.)

Since most products are used in open air, the results obtained in a vacuum may not be actual. In the first place, powder or liquid materials are hardly measured in a vacuum. The AC Series measure in open air, allowing evaluation in actual usage conditions. It's also easy to compare materials before and after processing for results corresponding to actual conditions.



- No vacuum required
 - Reducing initial and running costs

Conventional systems for measuring work function and ionization potential require a vacuum for measurement. The AC series can measure in open air without a vacuum. This reduces costs by reducing initial and running costs of equipment.



Widely used by researchers, with papers published worldwide exceeding **1,600**

The AC Series are used for research and development in a wide range of fields, with results published as papers. More than 1,600 papers* have been published worldwide.

Even today, they're in use by researchers around the world to compile papers.
*Until June 2018



The Principle of the AC Series

Operating principle

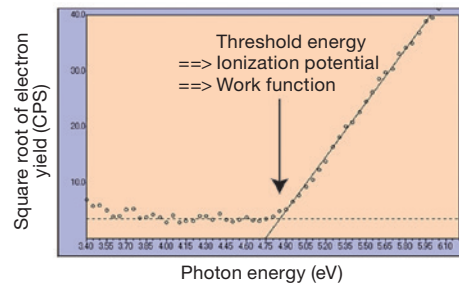
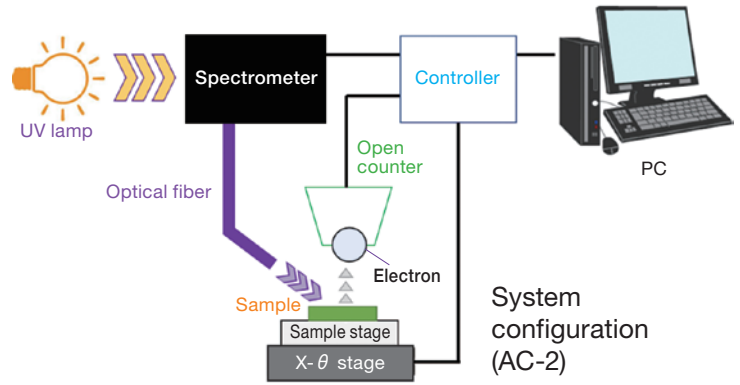
Ultraviolet photons emitted from an ultraviolet lamp undergo wavelength selection (energy selection) in a spectrometer before being focused on the surface of a sample placed on the sample stage (in open air). Photoelectrons discharged due to the photoelectric effect (phenomenon in which electrons are discharged from a material surface when the material absorbs light) are counted by an open counter, and the count is processed and the results displayed on a PC. The wavelength λ of the ultraviolet radiation is converted into the light energy E using the following equation.

$$E = h\nu = \frac{hc}{\lambda}$$

(h : Planck constant, ν : frequency, c : speed of light)

The value of the threshold energy of photoemission, which corresponds to the ionization potential, is determined from the energy of an interesting point between the background line and the extrapolated line of the linear portion of square root plots of the photoemission yield. If the sample is metal, the value of the threshold energy of photoemission corresponds to the work function.

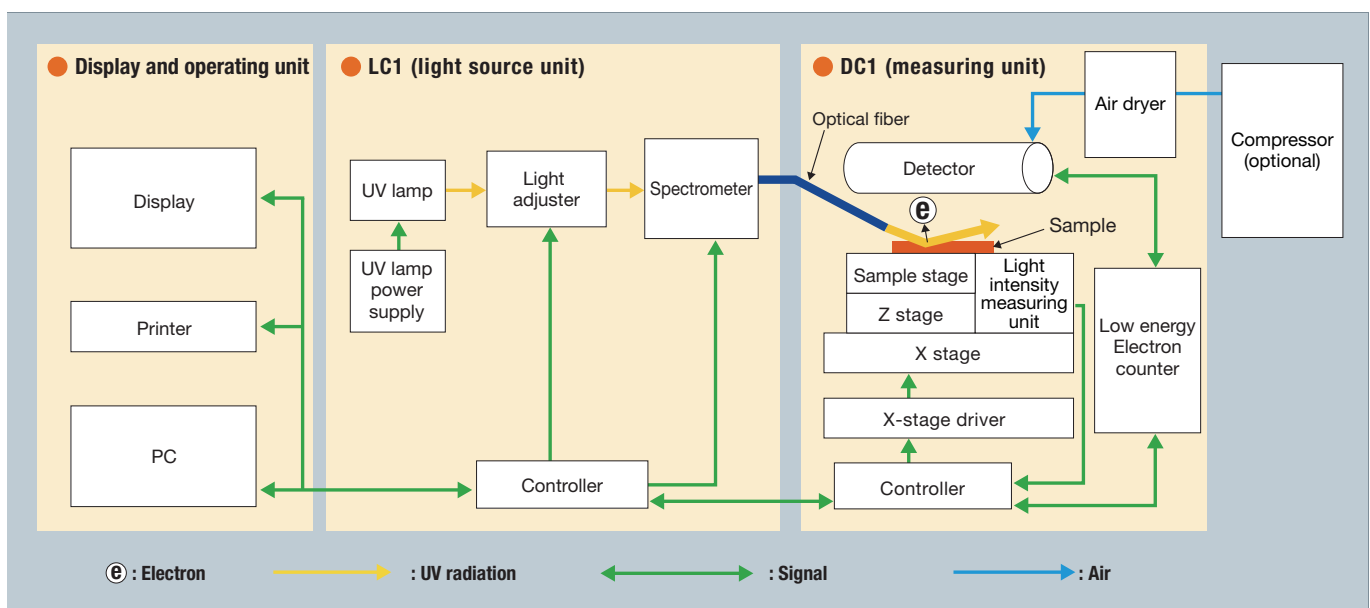
*CPS: Counts per second; unit of electron count rate
(number of electrons counted per second)



PC screen
(A measurement sample of AC-2)

System configuration (AC-2)

A system configuration sample of AC-2 is shown in the following diagram. The whole equipment is divided into the display and operating unit, LC1 (light source unit), and DC1 (measuring unit). Furthermore, the spectrometer of AC-3 and the sample stage of AC-5 are not the same as those of AC-2.



Electron counting principle by the open counter

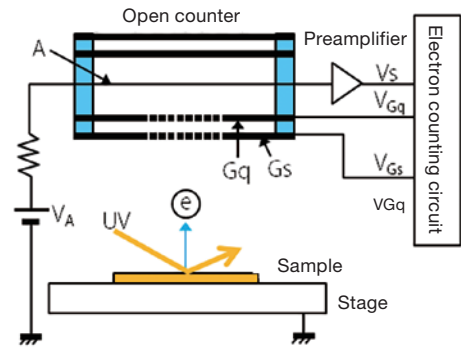
The open counter repeats the following operations to count electrons:

1. Electron generation

Electrons are discharged from the sample when bombarded by UV radiation. An electric field is produced on a suppressor grid (Gs) to which a voltage is applied. The electrons are directed toward the open counter.

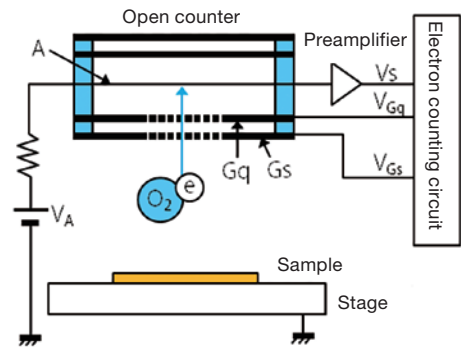
Symbols in the diagrams:

A : Anode Gs : Suppressor grid e^- : Electron
 Gq : Quenching grid UV : Ultraviolet radiation



2. Electron movement using oxygen as a carrier

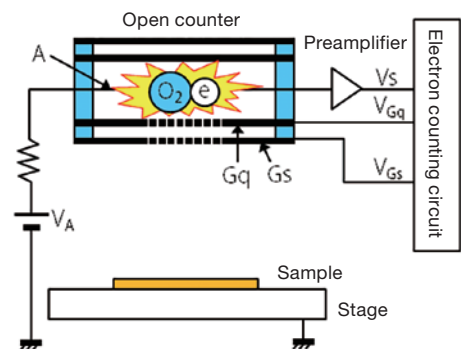
The electrons bind to oxygen (O₂), forming negative oxygen ions that drift toward the open counter. After passage through the Gs and Gq grids, the electrons are carried to the anode (A) to which a high voltage is applied. The electrons are stripped from the oxygen (O₂) by the nonuniform electric field close to the anode.



3. Electron detection by electron avalanche

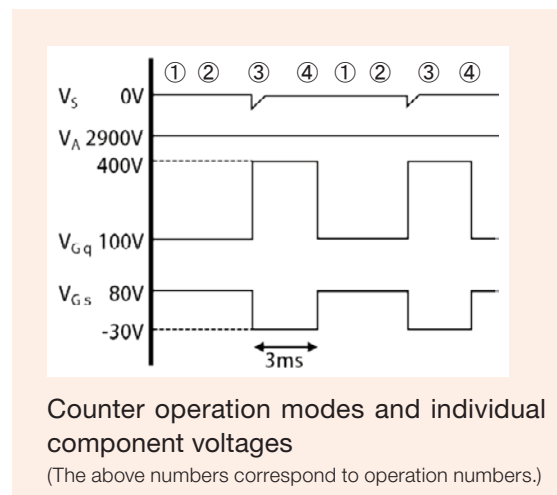
The electrons are accelerated in the nonuniform electric field, causing an ionizing "electron avalanche (discharge phenomenon)" due to collisions with surrounding molecules. The large number of the electrons generated* are detected as discharge pulse signals by the anode. The signals detected are amplified by a preamplifier.

*The electron avalanche amplifies each individual electron into 10⁵ to 10⁷ electrons.



4. Electron avalanche quenching

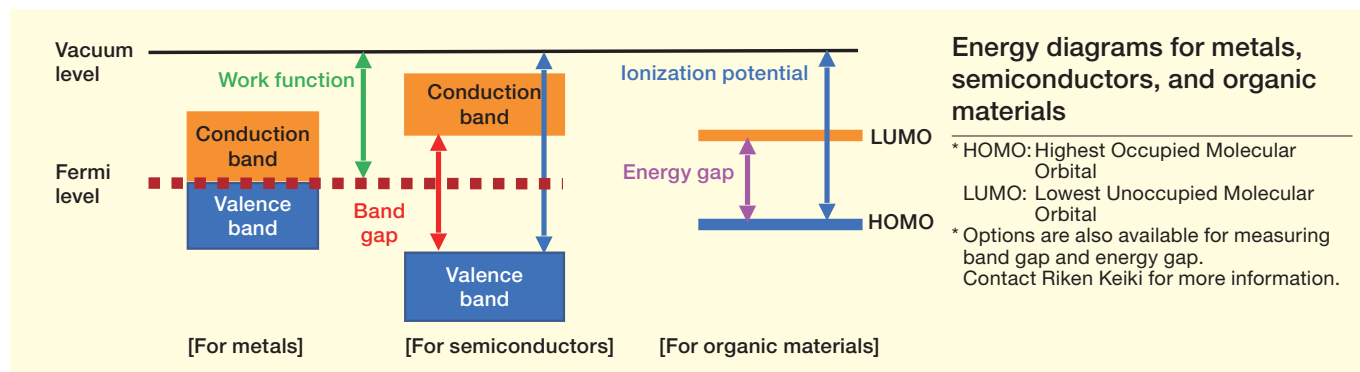
Cations generated in the vicinity of the anode interfere with electron detection, so the grid voltage is varied after electron pulse detection to stop the electron avalanche. The sampling grid captures the cations generated and prevents electrons from entering the detector. The conditions are then restored to their original state.



The Principle of the AC Series

Energy diagram

The energy diagram illustrates the orbits and energy of electrons inside a material. It's a fundamental diagram for understanding how electronic devices work.



The values measured by the AC Series (photoelectric emission threshold energy) are work function (for metals) and ionization potential (for semiconductors and organic materials). This therefore reveals the valence band upper-end energy for metals and semiconductors, and the HOMO energy for organic materials.

Comparison with other principles

Comparisons with other principles for measuring work function and ionization potential are given below.

Principle name	Photoemission yield spectroscopy in air (PYSA)	Ultraviolet photoelectron spectroscopy (UPS)	Cyclic voltammetry (CV)
Principle	The total number of emitted electrons per incident photon is counted as a function of photo energy.	The kinetic energy distribution of the emitted photoelectrons (<i>i.e.</i> the number of emitted electrons as a function of their kinetic energy) is recorded using vacuum UV (21 eV) radiation.	A voltage (potential) is applied to samples in the electrolyte. The current value corresponding to the potential is measured.
Objects to be measured	Solids, thin films, powders, liquids	Solids, thin films	Molecules in liquid
Example measurements			
Measurement environment	In open air	In vacuum	In liquid
Advantages	<ul style="list-style-type: none"> • Minimal damage, with high repeatability, even for the same organic samples • Even electrodes and organic materials can be measured. (Results can be compared.) • Absolute value measurement • Operation is simple, enabling measurement by anyone. • Short measurement time (several minutes) 	<ul style="list-style-type: none"> • Even electrodes and organic materials can be measured. (Results can be compared) • Wide measurement range (0 eV to 21 eV) 	<ul style="list-style-type: none"> • Easy measurement • Relatively short measurement time
Disadvantages	<ul style="list-style-type: none"> • Narrow measurement range (3.4 eV to 7.0 eV) 	<ul style="list-style-type: none"> • Susceptible to damage from intense UV radiation • Operation is complex, requiring specialist knowledge • Long measurement time (several hours) 	<ul style="list-style-type: none"> • Results cannot be compared when materials are insoluble in the same solvent • Relative measurement • Low reliability • Data analysis is difficult

Uses for the AC series

Material selection (screening)

⇒ Case study 1 (p. 8)

Applications: Organic electroluminescent devices, organic transistors, organic thermoelectric transducer, nanocarbon materials, graphene, fullerene, carbon nanotubes, transparent conductive films, quantum dots, nanoparticles, metal electrodes

Charge transfer characteristics can be predicted to select effective materials by plotting energy diagrams using the work function and ionization potential measured using the AC Series.



Indices for new material development

⇒ Case study 2 (p. 8)

Applications: Photocatalysts, fuel cells, lithium-ion batteries, organic solar cells, inorganic solar cells, dye-sensitized solar cells, Perovskite solar cells

Charge transfer characteristics can be predicted to use as indices for new material development by plotting energy diagrams using the work function and ionization potential measured using the AC Series.



Material surface film thickness measurement

⇒ Case study 3 (p. 9)

Applications: Silicon devices (pre-processing), lead frame bonding wires, metal/oxide film deposition hard disks

Graph slope and discharge electron counts measured using the AC Series can be converted into film thickness to measure material film thickness.



Electron state analysis of liquid samples

⇒ Case study 4 (p. 9)

Applications: Food, chemicals, cosmetics, pharmaceuticals, medicine

The AC Series can measure even liquids and powders in open air, enabling electron state analysis in actual conditions.



The AC Series Measurement Case Studies

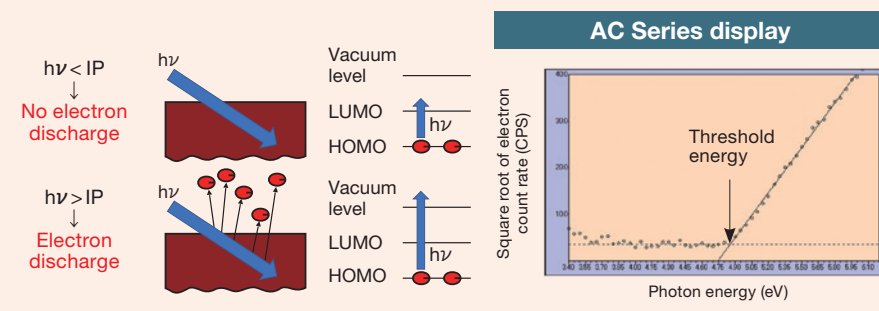
Material selection (screening)

Case study 1: Ionization potential measurement of organic electroluminescent materials

Manufacture of organic electroluminescent devices requires selection (screening) of optimum charge injection materials for charge injection into luminescent materials. Charge transfer at the material interface is important here, and ionization potential forms a key factor in evaluating materials. The AC Series are able to measure ionization potential quickly and easily in open air.

What the AC Series reveals (Explanation of phenomena)

Irradiating a material with UV radiation increases the energy of electrons exactly by the energy of the UV radiation ($h\nu$). Electrons are emitted from the material if the electron energy exceeds the vacuum level. The ionization potential (IP) can be estimated from the electron emission threshold energy.



Ionization potential of organic thin films

Ionization potential for metals differs between vacuum and in open air due to surface oxidation but is relatively consistent for organic materials. These are the results of measuring organic materials in open air and vacuum.

	In open air	In vacuum
Alq3	5.84eV	5.8eV
a-NPD	5.50eV	5.4eV
CuPc	4.99eV	5.2eV

*In open air: AC Series
In vacuum: Measured using ultraviolet photoelectron spectroscopy

Indices for new material development

Case study 2: Searching for fuel cell materials (energy)

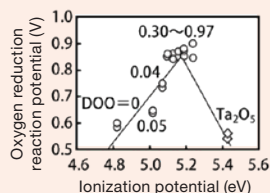
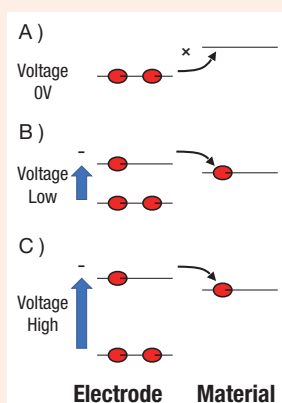
A breakthrough in the performance of renewable energy devices such as artificial photosynthesis, solar cells, photocatalysts, fuel cells, and storage batteries has become a pressing need to curb global warming. This has produced strong demands for development of new materials differing from conventional materials. For example, searching for materials to replace platinum for the cathodes of fuel cells traditionally involved wide use of CV measurement. Using the AC Series which are capable of measuring solid materials enables efficient material searching.



What the AC Series reveals (Explanation of phenomena)

Electron transfer from electrode to material causes a chemical reaction. You can see the following using the AC Series.

- A) Electrode HOMO < Material LUMO
=> No electron transfer
- B) Apply voltage (low) to electrode
Electrode HOMO > Material LUMO
=> Electron transfer (High efficiency example)
- C) Apply voltage (high) to electrode
Electrode HOMO > Material LUMO
=> Electron transfer (Low-efficiency example requiring high voltage)



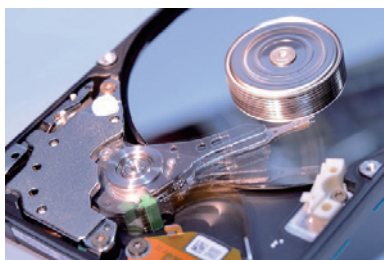
Correlation between ionization potential and oxygen reduction reaction voltage (E_{ORR}) of fuel cell

A. Ishihara, M. Tamura, K. Matsuzawa, S. Mitsushima and K. Ota, J. Fuel Cell Sci. Technol, 8 (3), 031005

Material surface film thickness measurement

Case study 3: Silicon oxide film thickness measurement

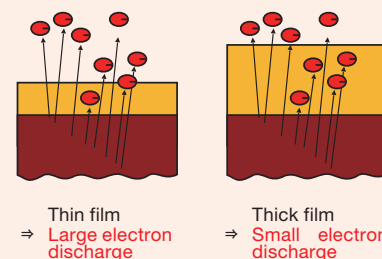
Semiconductor materials require confirmation of film thickness uniformity. However, steady improvements with integration in recent years have resulted in thinner films, making thickness measurements by conventional methods (FT-IR) difficult. The AC Series can measure film thicknesses at an angstrom level by using the electron permeability of thin films. And it also allows film thickness evaluation in high integration.



What the AC Series reveals (Explanation of phenomena)

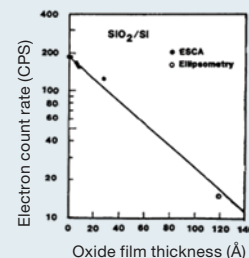
The volume of electrons discharged from a material varies depending on the thickness of the silicon wafer.

With thinner films, a greater volume of electrons is discharged; with thicker films, the surface film forms an obstruction, and a smaller volume of electrons is discharged. Measuring the electron discharge for a known film thickness at a constant ultraviolet intensity and plotting this on a graph enables determination of unknown film thicknesses.



Correlation between silicon wafer surface oxide film thickness and electron count rate

We see clearly that the electron discharge decreases as the oxide film thickness increases. Allows measurement in open air even of films measuring just a few Å in thickness.



M. Uda, Jpn. J. Appl. Phys., 24 (1985) 284

Electron state analysis of liquid samples

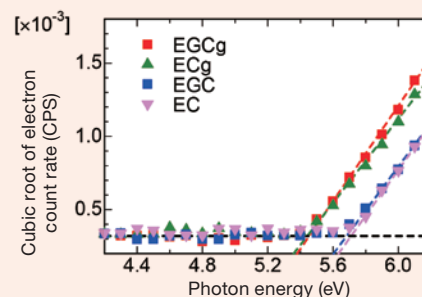
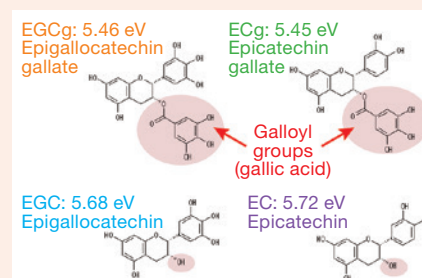
Case study 4: Measuring catechins in water

The AC Series are capable of measurements in open air, which allows electron state analysis for liquid and powder samples and presents applications across a wide range of fields, including food, chemicals, cosmetics, medicine, and pharmaceuticals. Catechins forming the astringent component of green tea are widely reported to exhibit biological activity. The following experiments show that catechins, which was reported to have a high biological activity, showed a low ionization potential.



What the AC Series reveals (Explanation of phenomena)

Biological activity including antioxidant, anticancer (suppressing cancer cell growth), antibacterial, and antiviral (deactivating) properties is generally reported to be higher in catechins with galloyl groups (gallic acid). If we use the value for standard bottled green tea as a guide, measuring the ionization potential of powdered catechins mixed with pure water reveals that catechins with galloyl groups have lower ionization potential. In practice, bottled green tea also contains chemicals in addition to catechins, which present issues. But using an Atmospheric Photoemission Yield Spectrometer provides information on electron states under normal daily life conditions.



D. Yamashita and A. Ishizaki, Anal.Sci., 32 (2016) 577

The AC Series Model Introductions

Model : AC-5

High-end AC Series model suitable for a wide range of scenarios



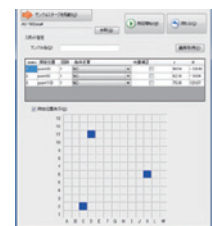
Main features

*Optional.

- The new sensor is capable of counting up to 4,000 photoelectrons per second.**
 Counts approximately twice the number of photoelectrons compared to the AC-2 or AC-3.
 Offers even greater accuracy.
- Large samples up to 180 × 180 mm can be mounted.**
 The large sample stage dramatically increases the size of samples that can be measured from the previous 50 × 50 mm (AC-2).
 Large samples can be measured in their current state.
- Specified-spot measurement allows measurement at any locations.**
 Specified-spot measurement allows users to specify a point on a sample for measuring work function and ionization potential.
- The sample changer* allows automatic measurements of up to 25 plate or powder samples.**
- The Xe (xenon) lamp* allows high-sensitivity measurement, even for materials like toner associated with low electron discharge.**



Large sample stage



Specified-spot measurement screen



Plate changer



Powder changer

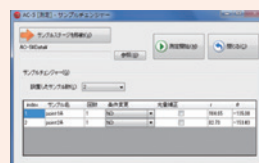
Measurement procedure

1. Start the system by following the on-screen instructions.



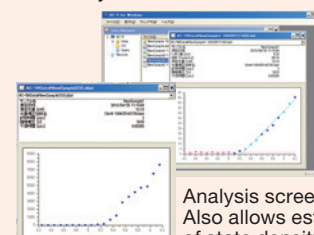
Guidance screen

2. Mount sample and start measurement.



Changer screen
 Allows the operator to set the name and number of measurement samples for each sample.

3. Data is displayed by analysis software.



Analysis screen
 Also allows estimates of state density.

Model : AC-3

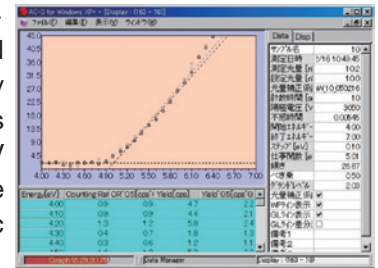
Allows measurements of up to 7.0 eV.



■ Features

- Allows measurements of up to 7.0 eV in open air.

The developed nitrogen-substitution-type specialized optical system is capable of irradiating samples with far ultraviolet radiation exceeding 6.2 eV—something previously deemed impossible due to absorption by atmospheric air. This enables measurements of up to 7.0 eV in atmospheric air. Also suitable for measurements of organic materials



AC-3
PC screen display

Model : AC-2

Model intended for use in academia



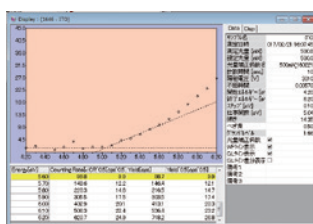
■ Features

- AC Series model most widely used worldwide for ionization potential measurement

Numerous papers have been published worldwide based on data obtained with the AC-2.

- Maximum light intensity 500 nW

Also capable of measuring work functions of conductive oxide materials such as ITO (indium tin oxide)



AC-2
PC screen display

Research organizations currently using the AC Series (partial list)

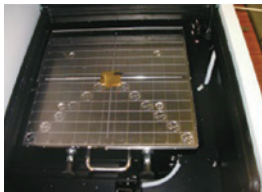
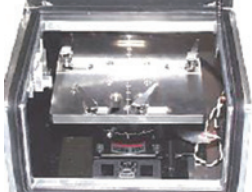

University of Tokyo, Kyoto University, Nagoya University, Yamagata University, Kyushu University, Riken, National Institute for Materials Science, Stanford University (USA), Princeton University (USA), Strasbourg University (France), Fraunhofer Institute (Germany), Humboldt University (Germany), Peking University (People's Republic of China), South China University of Technology (People's Republic of China), Industrial Technology Research Institute (the Republic of China), Korea Electronics Technology Institute (Republic of Korea), Kyungpook National University (Republic of Korea), VISTIC (Thailand), IMRE (Singapore), CSIRO (Australia), KAUST (Saudi Arabia)

(*Based on papers published)

*Data from the AC series has contributed to more than 1,600 papers, with numerous instances of use in research by corporate research organizations.

Easily searched for on the web using the keywords "Rikenkeiki, AC-2, AC-3".

Comparison of AC Series Atmospheric Photoemission Yield Spectrometer Specifications

Model	AC-5	AC-2	AC-3
Measurement principle	Photoemission Yield Spectroscopy in Air (Low-energy electron counting)		
Electron detector	Open counter		
Photoelectron measurement energy scanning range	3.4 eV to 6.2 eV (364 nm to 200 nm)		4.0 eV to 7.0 eV (310 nm to 177 nm)
Light intensity measurement energy scanning range	3.4 eV to 6.2 eV (364 nm to 200 nm)		4.0 eV to 7.0 eV (310 nm to 177 nm)
Repeatability (standard deviation)	Work function 0.02 eV (sample: metal plate)		
Measurement time	Standard time required for work function measurement: Approx. 5 minutes		
Maximum count rate (CPS: Number of electrons measurable per second)	4,000CPS		2,000CPS
UV lamp	D2 lamp		
Minimum light intensity	Below 1.0 nW (at 5.9 eV)	Below 5.0 nW (at 5.9 eV)	
Maximum light intensity	Over 500 nW (at 5.9 eV)		Over 100 nW (at 5.9 eV)
UV spot size	Below 4 mm × 4 mm (Varies with energy due to condenser lens chromatic aberrations.)		2 mm × 5 mm (No chromatic aberrations because light is condensed using a concave mirror)
Spectrometer	Grating-type monochromator		Nitrogen-substitution grating-type monochromator
Sample shape	180 mm × 180 mm (max.) Max. thickness 1.0 mm ±0.2 mm	50 mm × 50 mm (max.) Max. thickness 10 mm (max.), 1-point measurement	30 mm × 30 mm (max.) Max. thickness 10 mm (max.), 1-point measurement
Measurement location	Multiple locations can be specified on the sample stage for sequential measurement.	Measures sample center.	
Sample stage			
Operating temperature/humidity range	15°C to 35°C Dew point -30°C or higher, 60% RH or less	15°C to 35°C, 20% to 60% RH	
Power supply	100 V to 240 V AC, 50/60 Hz, 5 A (Max)		
Compressed air	High-purity air 0.2 MPa to 0.3 MPa, 0.2 L/min (measurement), 2 L/min (purging)	0.5 MPa to 0.7 MPa, 5 L/min	
High-pressure nitrogen	Not required	Not required	0.5 MPa to 0.6 MPa, 2 L/min (measurement), 5 L/min (purging)
External dimensions	AAC-5 LC (light source unit): Approx. 470 (W) × 500 (D) × 300 (H) mm AC-5 DC (measuring unit): Approx. 600 (W) × 500 (D) × 380 (H) mm (excluding rubber feet and other protrusions)	AC-2 LC1 (light source unit): Approx. 600 (W) × 450 (D) × 310 (H) mm AC-2 DC1 (measuring unit): Approx. 600 (W) × 450 (D) × 360 (H) mm (excluding rubber feet and other protrusions)	Approx. 740 (W) × 680 (D) × 1,080 (H) mm (including casters)
Weight	AC-5 LC (light source unit): Approx. 35 kg AC-5 DC (measuring unit): Approx. 50 kg	AC-2 LC1 (light source unit): Approx. 40 kg AC-2 DC1 (measuring unit): Approx. 50 kg	Approx. 120 kg
Certifications and Approvals	—	UL/cUL	—

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