

2023

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Recommended Citation

Ishaan Deepak Joshi, 'Applying Electron Spectroscopy In Forensic Chemical Analysis' (2023) 2 JJLR 1-11.

Available at www.jurynesia.com/vol-2-issue-4/.

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APPLYING ELECTRON SPECTROSCOPY IN FORENSIC CHEMICAL ANALYSIS

Ishaan Deepak Joshi¹

ABSTRACT

Spectroscopy is a forensic method that is commonly employed to identify and quantify the composition of a specific component in a given sample. Spectroscopy refers to the process of quantifying the absorption, emission, or scattering of electromagnetic radiation by atoms or molecules on a surface. Absorption refers to the process of electromagnetic energy being transferred to atoms or molecules. Emission, on the other hand, involves the movement of electromagnetic energy from one energy level to another, culminating in the emission of photons. Scattering occurs when light changes direction when it interacts with matter.

KEYWORDS

Spectroscopy, Forensic Science, Electromagnetic Radiation, Molecular Composition, Absorption, Emission, Chemical Analysis

I. THE PRINCIPLE

When a primary X-ray beam with a precisely determined energy hits the atoms in a sample, it causes the inner shell electrons to be expelled, and the energy of these expelled electrons is then measured.² The disparity between the energy of the incoming X-ray and the expelled electrons determines the binding energy (E_b) of the electron to the atom. The identification of the element involved can be achieved by utilising the dependence of the binding energy of the released electron on the energy

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² Siegel, J.A. 1997, 'Forensic Chemistry' in Macmillian Encyclopedia of Chemistry, Macmillian Company, New York.

of the electronic orbit and the element.³ Moreover, the binding energy is significantly influenced by the chemical form or surroundings of the atom, resulting in a noticeable chemical shift. This shift may be utilised to determine the valence state and precise chemical form of the atom.⁴ The term commonly used to describe this method is Electron Spectroscopy for Chemical Analysis (ESCA). ESCA, also known as X-ray photoelectron spectroscopy (XPS), is a widely recognised method used to accurately analyse the chemical composition of surfaces in various specimens. This approach is highly beneficial for analysing elements with low atomic numbers and surface contaminants.

The procedure is intricate and necessitates a relatively high level of vacuum known as ultra-high vacuum (UHV) settings. The ultra-high vacuum (UHV) conditions generally have a pressure below 10 to the power of -9 millibar. At ultra-high vacuum (UHV) conditions, the number of atoms per unit volume is approximately 1/1,000,000,000,000 of that in air due to the atmospheric pressure being just 1 bar. Surface analysis benefits greatly from this situation, since it facilitates the deposition of airborne molecules onto the surface, therefore altering its properties. The atoms adhere to the surface during a time span of 3 seconds, rendering them unanalysable due to insufficient duration for experimentation. The experiment necessitates ultra-high vacuum (UHV) conditions in order to allow for a sufficient duration of many hours to perform the experiment. The UHV chamber is initially prepared by evacuating it to a pressure of 10 to the power of -2 millibar using a rotary pump. Subsequently, a turbomolecular pump is employed to evacuate the system to a pressure of 10 to the power of -6 millibar. The vacuum chamber is contained within a hermetically sealed furnace and subjected to a temperature of around 180 degrees Celsius. The baking process last

³ Siegel, J.A. 2004, 'Accreditation of Undergraduate and Graduate Forensic Science Education Programs,' *Forensic Magazine*, Vol. 1, No. 3, pp. 2326

⁴ Skoog, D. A., Holler, J. & Nieman, T. A. 1998, *Principles of Instrumental Analysis*, 5th edn, Thomson Learning, Crawfordsville.

two days in order to eliminate any residual gas within the chamber, followed by a subsequent cooling period. This achieves the ultra-high vacuum (UHV) chamber at ambient temperature. The output is analysed by finding typical peaks and examining their respective regions. The equipment is connected to computers to facilitate data analysis. The adhesive procedure involves the evaluation of both the surface condition and composition. ESCA or XPS has offered forensic investigators a crucial instrument for identifying the origins and whereabouts of failure.

II. OVERVIEW

Electron spectroscopy for chemical analysis (ESCA), commonly referred to as x-ray photoelectron spectroscopy, was initially elucidated by Albert Einstein in 1905. Einstein proved that the energy of an electron released in photoemission is equal to the discrepancy between the energy of the incident photon and its binding energy. The fast advancement of ESCA occurred when scientists utilised x-ray photoemission to quantify the binding energies of core electrons.⁵ They discovered that these binding energies might change by up to 6 eV depending on the chemical state of the atom. This approach yields crucial data on the chemical impact on surfaces, rendering it very sensitive to surface properties. Additional spectroscopy methods, like atomic emission spectroscopy (AES) and atomic absorption spectroscopy (AAS), analyse absorption or emission based on energy.⁶ In contrast, ESCA determines the kinetic energy of electrons that are expelled by x-ray radiation.⁷

The ESCA is conducted utilising a synchrotron-based illumination source in conjunction with a specially built electron analyser. The predominant ESCA system employs 20-200 micrometre beams of either

⁵ Wagner, C.D., Riggs, W., Davis, L. & Moulder, G. 1979, Handbook of X-ray Photoelectron Spectroscopy, Perkin-Elmer Corp., Eden Prairie, MN, USA

⁶ Sabilia, J. P. 1988, Materials Characterization and Chemical Analysis, 2 edn, VCH Publishers, New York.

⁷ Seah, P. & Briggs, D. (eds) 1992, Practical Surface Analysis by Auger and X-ray Photoelectron Spectroscopy, Wiley & Sons, UK.

monochromatic aluminium K-alpha x-rays or polychromatic magnesium alpha x-rays. A single-coloured x-ray beam is generated by diffracting and concentrating a multi-coloured x-ray beam using a thin disc of naturally occurring crystalline quartz with a lattice structure.⁸ The wavelength of 0.8339 nm corresponds to a photon with an energy of 1486.7 eV. The monochromatic x-rays possess a diameter of 0.16 eV, whereas the ESCA system exhibits a high energy resolution of around 0.25 eV. Conversely, the polychromatic magnesium x-rays have a wavelength of 0.99 nm, which is equivalent to a photon energy of 1254 eV. The energy resolution of the device while employing a non-monochromatic x-ray beam is around 0.70 eV. Furthermore, crystals do not serve the purpose of diffracting x-rays, hence enabling the unhindered transmission of both primary x-rays and high-energy Bremsstrahlung x-rays to the surface.⁹

ESCA is extensively utilised in forensic laboratories. Its primary use lies in surface analysis, particularly in the qualitative determination of the components present in a sample. The estimation of the chemical environment around the atoms may be inferred from the chemical changes. This measurement is valuable for establishing the valence states of the atoms found in different components within a sample. Quantitative measurements may be obtained by assessing the intensity of the ESCA lines associated with each element.

III. MEASUREMENT AND CONTROL OF VARIABLES IN A SYSTEM

The system comprises a radiation source that emits primary X-rays, a monochromator to choose a certain wavelength, an energy analyser to separate the electrons produced by the samples based on their energy,

⁸ Siegel, J.A. 2000, *Collection and Chain of Evidence*, Academic Press Limited, London.

⁹ Ewing, G. W. 1985, *Instrumental Methods of Chemical Analysis*, 5th edn, McGraw-Hill, New York.

and a detector to quantify the intensity of the separated electrons.¹⁰ The analysis is conducted under conditions of high vacuum.¹¹

The ESCA technique is commonly employed for the analysis of diverse components, including inorganic substances, polymers, elements, cosmetics, teeth, bones, and numerous others. The surface composition, typically ranging from 1 to 10 nm, is examined to determine its empirical formula and identify any surface contaminants.¹² Line profiling is used to assess the uniformity of elemental composition over the top surface, while depth profiling analyses the composition at different depths.

The emitted photoelectrons from the sample are quantified for each kinetic energy value, resulting in the generation of a spectrum using equation 1. ESCA is employed to ascertain the bonding state and surface concentrations by utilising the fact that the binding energy of an electron is a chemical attribute particular to the element and orbital.¹³

IV. TECHNIQUES

The X-ray photoelectron spectroscopy (XPS), often referred to as electron spectroscopy for chemical analysis (ESCA), utilises the principle of the photoelectric effect to identify the chemical makeup of a surface. Special ESCA systems have been specifically developed to analyse volatile gases or liquids. These systems can handle samples at various temperatures and operate under a vacuum of around 1 torr. By utilising the known energy of a certain x-ray wavelength, one may ascertain the electron

¹⁰ Kuwana, T. 1980, *Physical Methods in Modern Chemical Analysis*, Vol. 2, Academic Press, London.

¹¹ Ingle, J. D. & Crouch, S. R. 1988, *Spectrochemical Analysis*, Prentice-Hall Int., New Jersey

¹² Schroder, E., Muller G. & Arndt, K. 1989, *Polymer Characterization*, Hanser Publishers, Munich.

¹³ Levy, P. S. & Lemeshow, S. 1991, *Sampling of Populations*. John Wiley and Sons, New York.

binding energy (BE) of each released electron by the use of the following equation, which is derived from Rutherford's research:

The equation (1) expresses the relationship between the energy of an electron (E) emitted during a transition between energy levels within an atom, the energy of the photon utilised (E), the kinetic energy of the emitted electron as measured by the electron (E), and the work function of the instrument (ϕ). The work function serves the aim of supplying additional energy required for the transmission of an electron from the surface of the specimen to the vacuum region. Every instrument possesses its own pre-established value.

Essentially, the examination of a sample involves three fundamental steps or actions. Initially, the sample is obtained from the source. Subsequently, the sample is prepared using various processes such as culturing, cleaning, or soaking, and then subjected to suitable methods for analysis. These approaches are mutually exclusive, although one can have a significant impact on the other in terms of photon binding and kinetic effects. During the process of analysis, mistakes may occur, and it is important for the analyst to be vigilant in recognising and preventing these errors. The chosen analytical approach should adequately account for the precision, responsiveness, and reliability required. Hence, the scientists should assess the current methodology and determine its acceptability.

V. PREPARATION OF THE SAMPLE

The solid samples for analysis should have dimensions ranging from 0.1 to 4.0 cm and possess extremely low vapour pressures. Initially, the samples undergo analysis, followed by the removal of the 20Å surface using a process called light sputtering, which is commonly referred to as

depth profiling.¹⁴ This ensures that the surface remains free from any organic or accidental contaminants. Forensic analysis requires a quality assurance programme to oversee the testing process and ensure that the methodologies used and the reported findings meet the standards of competency and auditing. The recommendations can be seen inside the trace evidence quality assurance guidelines (TEQAG).

VI. ANALYSIS EXAMPLE

During ESCA, a monochromatic x-ray beam is used to irradiate the sample. The photoelectric effect is responsible for the emission of the core electron(s) in the sample. The phenomenon can be elucidated by the observation that when a metal surface is exposed to light, electrons are emitted. The released electrons are detected with a cylindrical mirror analyser (CMA) detector. The provided kinetic energy is subsequently transformed into binding energies, enabling the determination of the constituent components. The energy spectra obtained demonstrate the relationship between binding energy and intensity. Utilising sensitivity factors can provide useful quantitative information about the elemental surface compositions through the analysis of peak intensities. ESCA or XPS is extensively utilised in forensic laboratories for the examination of adhesive joints and the acquisition of compositional data regarding the surfaces of the specimens. This is especially advantageous in the detection of impurities that might be responsible for the failure, places where bonding did not occur, and absence of adhesive. Furthermore, it also verifies if the failure occurs in the adhesive, the original substance, or at the interface.

VII. OUTCOME

¹⁴ Yacobi, B., Holt, D. B. & Kazmerski, L. 1994, *Microanalysis of Solids*, Plenum Press, New York.

The ESCA spectrum yields data on both the surface characteristics of the sample and the oxidation state (chemical environment) of the element. The strength of electron bonding is regulated by the chemical environment in which it is located. Atoms that have various chemical environments produce peaks with varying binding energies, which are known as chemical shifts. Furthermore, distinct chemical states may be disentangled by utilising peak fitting programmes, which provide the percentage composition of each unique state. When presenting the laboratory findings, it is important to ensure uniformity and consistency. The laboratory guides should include explicit documentation about the format, approved units of measurement, and calculating methods. All individuals participating in the investigations must possess the ability to comprehend the findings and effectively interpret them, elucidating their importance with utmost clarity. Furthermore, it is imperative that laboratory findings adhere to ISO (International Organisation for Standardisation) standards. This body mandates that the information provided must be succinctly unambiguous, highly precise, and immediately identifiable in the presentation of findings.

VIII. BENEFITS

Both the ESCA method and the Auger Electron Spectroscopy (AES) are surface analysis techniques. The CMA detector is utilised to examine the expelled electron in both methodologies. Furthermore, the ESCA scan yields analogous or equivalent data to AES. Nevertheless, ESCA possesses some benefits compared to AES, which has led to its recent adoption as a valuable supplementary technique to AES in the forensic investigation of biomolecules. For instance, the AES technique might provide detrimental electron bombardment to some materials that, conversely, are unaffected by the ESCA monochromatic x-ray bombardment beam. Moreover, the electron bombardment in AES encounters an issue of inducing charge accumulation in insulative

specimens, resulting in subpar analysis. The process of charging the material is not encountered in ESCA neutral analysis.

The energy resolution of ESCA is often superior than that of AES. This is very valuable for determining the binding energies of atoms in a molecular structure. Therefore, both the elemental composition and chemical bonding information are provided. ESCA has been extensively utilised in the semiconductor industry to examine the surfaces of organic materials, oxides, and polymers. Furthermore, it has been utilised in the advancement of plasma etching methodologies.¹⁵

IX. CONSTRAINTS

The ESCA technology is incapable of detecting the hydrogen or helium atom. It is not feasible to reduce the diameter of the x-ray beam beyond that of electron beams in this particular technology. The insufficiency has resulted in the spatial resolution of ESCA being inferior to that of AES. This inherent vulnerability has also prompted the development of a novel method called imaging XPS (iXPS). Modern spectrometers equipped with this functionality provide the opportunity to do parallel imaging. However, this is crucial since it gathers information on locations based on the dispersion properties of the hemispherical analyser. This further produces photos with a high level of detail. A magnetic objective lens has been recently implemented in the iXPS, resulting in improved sensitivity and spatial resolution. This advancement allows for the expansion of the new technology. Furthermore, the precision of quantitative analysis is restricted to around 4 percent. A high vacuum is essential for the system to prevent low-energy electrons from colliding with contaminants, since this might lead to reduced sensitivity.

¹⁵ Surface Chemical Analysis — Vocabulary, ISO 18115: 2001, International Organization for Standardization (ISO), TC/201, Switzerland

Detecting contaminants at the parts per million (ppm) or parts per billion (ppb) levels is not feasible.¹⁶

¹⁶ Yacobi, B., Holt, D. B. & Kazmerski, L. 1994, *Microanalysis of Solids*, Plenum Press, New York