# Spectral Analysis as Product of Historical Development of Our Knowledge

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## Abstract

**Already the first human beings observed their surroundings in order to use different materials for to fulfil their primitive life needs.They recognized different metals, first genuine and later produced by metallurgical procedures. The ability to distinguish the properties of different materials enabled that chemistry as scientific branch was eventually created. The personalities who initiated its formation and development will be dealt with. For to rate the quality of investigated materials and especially their quantity, the till now used term of concentration was introduced and their determination represented a great challenge leading to the creation of analytical chemistry. Its principles reside in the determination of the relation between the value of the so called analytical signal (a well measurable physical quantity, e.g. electrical, optical, nuclear, mass, volume) and the feature which has to be determined (what, how much, where, how). This procedure represents the unevitable calibration process crucial for each analytical procedure.**
**One of the most advantageous analytical signals is represented by the emitted or absorbed intensity of electromagnetic radiation measured at an appropriate wavelength representing the basis for the broad family of spectroanalytical methods.**
**Original texts concerning the first description of spectrochemical analysis will be reproduced and its achievments for the culture development will be presented.**

**Key words:** *Analytical chemistry – history, personalities. Analytical signal, Analytical calibration, Optical methods, Spectral analysis, Position in culture*

## Introduction

In order to improve their life conditions the first primitive intelligent beings of homo sapiens species have allready been interested in their environment. They had to distinguish between objects available for food (edible – poissoneous), dress, decoration, hunt, defence, or to decide whether the given stone can be used as building material, for production of different tools, glass and later even for to obtain useful metals. The knowledge of these and many other properties made it posible to divide objects with similar properties in generalized groups and to achieve their categorisation presenting a first assumption for the origin of only many thousand years later created scientific approach to evaluation of simple investigations and finding relations leeding to discovery of new basic knowledge.

The whole existence can be divided in two most general categories: *nature* and *culture.* where the nature is represented by the collection created by evolution (or according to theological notion by God) without any influence of man, whereas the culture contains all results of human activities. According to this basic definifion the last can be further divided in material (industry, mining, communications, dwelling, architecture, agriculture etc.) and spiritual (polity, religion, law, literature, music, fine arts and last but not least: science) culture. In spite of this accepted basic division art is very often erroneously presented as the only content of culture.

## Development of science

What does science as immanent part of culture represent, what is its content, task and aim? This questions can be according to my notion answered for short as follows: *Science is the part of culture which gives answers on questions put by nature and human society and categorizes them in order to find their relations leading to new knowledge.* In consent with this approach we distinguish basicly between natural (e.g. chemistry, physics, biology, geology) and social (e.g. philosophy, politology, theology, linguistic) sciences. The formation of natural sciences represents a long period of the cultural development coming considerably later after the already well established existence of some social sciences like philosophy, war science, religion etc. A basic break leading to the origin of natural sciences can be stated in connection with the discovery of metals possessing new useful properties helping the improvement of life level, with other words with the formation of metallurgy. When we do not count different antic attempts made by some Greek and Roman philosophers, (e.g. Herakleitos from Ephesos, cca 540-480 B.C.; Archimedes, 287-212 B.C.; Titus Lucretius Carus, 96-55 B.C.) the first attempts of this endeavour can be observed in Middle Ages (e.g. Albertus Magnus 1193-1280, on Nov. 15 1931 even proclaimed saint) the very beginning of the development in natural sciences oriented on chemical problems can be dated first in the 16$^{th}$ century mainly in connection with mining and following preparation of metals. These activities led also to the definition of concentration describing how much metal can be produced from a given weight of ore which practical expression has survived till today and this in spite of the fact that it has no thermodynamic basis and cannot be correctly used to statistical and/or thermodynamical calculations. In the connection with the origin of scientific approach to the solution of different problems the work of Saxon native, later pharmacist in Bohemian Joachimsthal (Jáchymov) and a famous specialist in metallurgy Georg Bauer named Agricola, (1494-1555), author of significant books entitled: *De re metallica* (On metals), as well as Philippus Aureolus Theophrastus Bombastus von Hohenheim named Paracelsus (1493-1541) as founder and main representative of the so called *iatrochemistry* have to be mentioned. In the Middle Ages a great role was played by alchemy which, it is true, has found neither the *philosopher's stone* enabling the gold production, nor the *elixir vitae* ensuring everlasting life but it discovered a multitude of precious knowledge on chemical properties of many materials and so prepared a broad fundament for the creation of chemistry as scientific branch. The very origin of chemistry was, however, conditioned first in the 18$^{th}$ century by several important discoveries among which at leas the following have to be mentioned: The law of mass and energy preservation formulated by Mikhail Vasilevich Lomonosov (1711-1765), the refute of flogiston theory by discoveries of Antoine Laurent Lavoisier (1743-1794), the law of permanent proportions formulated 1799 by Joseph-Louis Proust (1754-1826) and the law of multiple proportions derived on the basis of his atomic theory by John Dalton (1766-1844).

## Analytical chemistry – its content and tools

A further necessary differentiation of chemistry led to the origin of inorganic, organic, physical, technical and what is the object of our interest – analytical chemistry. Its foundation is in general connected with the swedish chemist Jöns Jacob Berzelius (1779-1848) despite the fact that the first complete description of an analytical procedure has originated already from the ancient greec geometer, astronomer and inventor Archimedes who determined the correct composition of the golden crown made for Heron, the tyrant of Syracuse by its weighing in air and in water.

The tools of analytical chemistry in the Berzelius' time were restricted and consisted mainly in the formation of coloured compounds which served mainly for the identification of different components and deposits which weight was used for quantification purposes. Some later also voluminometric methods were introduced. Detection limits of these procedures did not exceed some hunderth parts of percent and all below this content was included under general term of traces.

What the activities of recent analytical chemistry consist in? In consent with its most general content, analytical chemistry as science gives answers on the following questions concerning chemical properties of matter: What? (qualitative analysis), How much? (quantitative analysis), Where? (local and structural analysis) and How? (speciation analysis). All analyses are performed in order to attain following two aims: Chemical characterization or Chemical control. In the case of characterization we have to do with the analysis of materials which composition is practically unknown and one has to determine as many components as possible and this in the broadest concentration range (e.g. Moon samples), meanwhile at the control one has to do with samples of practically known kind (e.g. steel, food-stuffs) in which only some components have to be determined and these even only in a relatively short concentration range prescribed by corresponding industrial standard determining their classification in a given quality group and permitted composition. The aim of chemical analysis which has to be performed is so determining for the choice of appropriate analytical method. In the case of characterization we use methods possessing multicomponent ability enabling the determination of the greatest number of components, excellent detectability and broad analyzable concentration range without any special stress on economic parameters as duration and price. Its accuracy does not play a significant role too and in some cases we are satisfied with only approximate data. On the other side in the case of analyses performed for chemical control the used method has to present high accuracy for the determination of only some demanded components and these even only in a relatively short prescribed concentration range often without any special stress on the detection power but its economical parameters, mainly duration and price have to be low.

The unity of analytical chemistry as scientific branch is given by the common principle of all analytical method consisting in the relation between analytical signal and the feature (what, how much, where, how) which has to be determined. Under the expression "*analytical signal*" we understand the value of a well measurable physical magnitude having relation to the sought feature which relation is of empirical character and it must be in all cases determined on empirical way presenting the crucial point of each analysis called analytical calibration. Owing to the empirical determination of this relation its character is stochastic in spite of the used description of its mathematical presentation as "*analytical function*". Despite of sometimes in the literature presented allegation on existence of calibration free analytical methods (e.g. gravimetry, coulombmetry) there do not exist any analytical procedure which would not need calibration. So in the case of gravimetry calibration is represented by values of gravimetric factors based in principle on relative atomic weights which are determined experimentally and their value has been regularly precised by IUPAC. The same situation is also with the value of Faraday's number serving as calibration factor at coulombmetric measurements. In this connection it is fully irrelevant if the calibration must be performed often directly by the operator or it issues from published data obtained by fully independent authority, it depends only on the ruggedness of the used analytical procedure representing its resistance against changes of experimental conditions in difference to its selectivity describing its resistance against the presence of concomitants contained in the sample beside the analyte which has to be determined.

In the consent with the presented point of view based on the definition of analytical signal it is obsolete to divide analytical methods in chemical, physicochemical, or physical ones, because all measured analytical signals (including gravimetry – mass, titration – volume etc.) are represented by physical magnitudes. In the same way a division in so called *classical* and *instrumental* analytical methods has no sense. Balance or burette are namely also instruments. The most logical division of analytical methods can be therefore based on the character of the used analytical signal (e.g. gravimetric, voluminometric, electrical, optical, nuclear). Physical magnitudes can be of *scalar* (their value is given only by one indication, e.g. mass, volume, amount of particles) or *vectorial* (their value depends on at least one additive variable, e.g. density on the temperature, diffusion current on the potential, intensity of electromagnetic radiation on the wavelength) where the last magnitudes used as analytical signal give more information. The value of an appropriate extensive (depending on the amount of the investigated substance or action) vectorial magnitude arranged in dependence on the ascendent value of a corresponding intensive (independent on the amount of the investigated substance or action) magnitude represents in general its spectrum (appearance of gravel pebble in dependence on their diameter – granulometric spectrum, important for the quality of concrete mix; dependence of the sound intensisty on the frequency – sound spectrum, important for the determination of the tone hight and quality; dependence of the electromagnetic radiation intensity on the wavelength – optical spectrum, which importance will be yet object of a more detailed investigation).

## History of light investigation

After this comparatively extensive but according to my oppinion for the correct understanding of the further text necessary introductory chapters we can continue with the own content of my lecture devotet to spectrochemical methods.

According to biblical description light represents the first object of the world creation. It means that to this phenomenon by means of which we gain by visual reception the greatest amount of information about our surrounding, the humanity has since its origin devotet extraordinary importance. In the original primitive conceptions natural light sources (Sun, Moon, rainbow, fire) were regarded as deities and even in Christianity light has been used as identical with God, e.g. John 1, 8: *"He* (John the Baptist, remark E. P.) *was not himself the light; he came to bear witness to the light. The real light* (Jesus, remark E. P.) *which enlightens every man was even then coming into the world".* Only after having gathered and systemized sufficient knowledge enabling the creation of scientific approach to the valuation of this phenomenon, it means approximately at the beginning of the 17th century more comprehensive knowledge also on the nature of light was possible.

Significant contribution to the elucidation of the light nature is the creation of corpuscular theory in 1672 by English physicist, mathematician and astronomer Isaac Newton (1643-1727) according to which light beam is considered as a stream of small material particles, later designated as photons which propagate from the source with a given velocity, having definite mass and quantity of motion. Danish astronomer Olaus Rømer (1644-1710) proved on the basis of astronomical observations (eclypses of Jupiter's moons) in 1676 Newton's assumption that the light indeed propagates with final velocity. The corpuscular theory was able to explain the linear propagation, reflection and refraction of light but its interference, diffraction and polarization remained unexplaned. Practically all properties of the light (with exception of polarization) could be explained by the undulation theory elaborated in 1678 by Dutch mathematician, physicist and astronomer Christian Huygens (1629-1695) presenting the light as longitudinal undulation similar to the sound. A break in the explanation of light propagation properties inclusive polarization was finally achieved by French physicist Augustin-Jean Fresnel (1788-1827) by having assumed light as transversal vibration.

A new approach to the explanation of the light nature is represented by electromagnetic theory published 1873 by the English physicist James Clerk Maxwell (1831-1879) according to which the visible light is only a part of electromagnetic radiation covering only a small range of wavelengths

(cca 400-800 nm) with continuation through ultraviolet, X ray and γ radiation having shorter and infrared, microwave, radio etc. radiation with longer wavelengths. Electromagnetic radiation of all wavelengths propagates in vacuum with a constant velocity and corresponds to transversal vibration of electrical vector and perpendicularly vibrating magnetic vector which phenomenon can be described by after Maxwell named mathematical equations.

According to the presented descriptions electromagnetic radiation possesses both – corpuscular as well as wave properties. On the basis of some disagreement between mathematical description of black body radiation proposed by English physicist Rayleigh (Lord John William Strutt, 1842-1919) and mathematician Jeans (Sir James Hopwood, 1877-1946) and its experimentally measured density as dependent on wavelength German physicist Max Karl Ernst Ludwig Planck (1858-1947) determined that radiation is not emitted continuously but by discrete particles named photons which energy is according to famous German physicist Albert Einstein (1879-1955) equal to $E = h.v$, where $v$ is the frequency of the radiation and $h$ represents the Plank's constant equal to quantum of action (product of work and time – F: action, - D: Wirkung, - R: действие, - E: acción, - H: hatás - Sk: účinok, unit: J.s, the same like for moment of movement). This equation represents an art of connection between corpuscular (energy of photon) and wave properties (frequency) of electromagnetic radiation. Since the frequency $v$ of electromagnetic radiation is not quantified, the energy of photons can gain in difference to often presented wrong application of quantum properties any arbitrary not quantified energy. This fact has not been emphasized with necessary stress by showing that quantified and constant is the action of one cycle independently on the frequency. This important basic statement that one cycle of electromagnetic radiation cannot be further divided which knowledge makes easily to understand the determination of resolving power of optical instruments. It confirms so the Rayleigh's experimentally proposed condition of one wavelength difference and in spite of this important new statement has till now not been generally applied. It has therefore been subject of my more comprehensive investigation with hope that its results will be soon presented. Electromagnetic radiation can be so specified by following two important basic properties: 1./ It propagates in vacuum with velocity independent on wavelength. 2./ The action of one unique cycle does not depend on wavelength and equals to Planck's constant. The second property has till now not been properly postulated and incorporated in the system of physics.


## History of spectroscopic investigations


In spite of the fact that rainbow as natural phenomenon had been known, admired and even adored since ancient days, one of the first scientific personalities who dedicated their life to spectral investigations of light was the Czech physician interested deeply also in physiology, mathematics, mechanics and optics Johannes Marcus Marci de Cronland (1595-1667) who published 1648 in Prague his book "*Thaumantias liber de arcu coelesti deque colorum apparentium natura, ortu et causis*" (Thaumas' doughter – [Iris, Greek godess of rainbow, remark E. P.] – book on rainbow, as well as nature, origin and reasons for appearance of colours) in which he described the creation of colours by refraction of white light on glass prism what represents the first information on light spectrum. This basic discovery is in literature often incorrectly ascribed to Isaac Newton who published the results of his investigation in his letter to the Royal Society only in 1672.

A significant progress in the development of our knowledge on electromagnetic radiation was achieved by investigations of sunlight spectrum, better said, only of its visible part represented by successive appearance of blue through green, yellow, orange to red colour. As beginning of visible spectrum is generally used to mention the violet. Violet is, however, only blue of low intensity which is perceived by human eye similarly like non spectral purple represented by mixture of blue and red which is as consequence of unsatisfactory colour education often also indicated as violet. Similarly, brown colour corresponds to low intensity orange. German physicist Joseph Fraunhoffer (1787-1826) described in sunlight spectrum after him named dark lines (1814) which had been observed already before him in 1802 by English chemist William Wollaston (1766-1828). These scientists were,

however, not able to explain their origin until English optician Sir David Brewster (1781-1868) presented (1820) on the basis of his results obtained with light absorption in different gases a hypothesis that Fraunhoffer's lines could be caused by presence of gases in the Sun atmosphere what presents the first suggestion of absorption spectral analysis, whereas the first attempt connected with emission spectral analysis was done in 1834 by English physicist and chemist William Henry Fox Talbot's (1800-1877) who investigated flames coloured by lithium and strontium, further in 1844 by Caselmann who described the influence of the composition of solution in which electrodes had been plunged before their use for the production of electrical arc, on the colour and intensity of the emitted light, as well as by some other scientists. Owing to several unsolved problems e.g. concerning the impossibility to ascribe some lines to some elements, like the extremely bright, practically omnipresent yellow sodium lines were ascribed to water or to burning sulfur. The mentioned scientists were, however, with all the obtained results not able to apply them in analytical chemistry instead of the complicated and slow wet analysis as a progressive method ensuring much better detectability and universality, capable to detect and determine practically all elements.

As the real origin for the application of spectra for chemical analysis and so for the formation of scientifically based spectrochemistry the formulation of results obtained by German physicist Gustav Robert Kirchhoff (1824-1887) and chemist Robert Wilhelm Bunsen (1811-1899) can be considered. Let us therefore present some original texts describing this event:
On the 20th Oct. 1859 Du Bois-Reymond presented to the Royal Prussian Academy of Sciences in Berlin Kirchhoff's letter from which we literally cite the relevant part: *"At the occasion of common investigation performed by Bunsen and myself .... on spectra of coloured flames it was for us possible to determine the qualitative composition of complicated mixtures from the look upon the spectrum of their soldering lamp flame."*. Some weeks later, on the 11th Dec. 1859 in the second Kirchhoff's letter was written: *"According to investigations performed by Wheatstone, Masson, Angström and others, it is known that in spectrum of electrical spark bright lines are found and they are dependent on the nature of metals between which the spark runs and it can be presupposed that these lines agree to those which would be formed in a high temperature flame if the same metals in a suitable form were put in. I investigated the green part of spectrum of light produced by electrical spark between iron electrodes and I found in it a great number of bright lines which seem to coincide with dark lines in the Sun spectrum."*. This statement was in the presented letter formulated also in the following form: *"From these investigations I attained now through a very simple theoretical consideration to a general sentence..... which describes a property of all bodies concerning their emission and absorption of heat and light"* what presents the basic, after Kirhoff named low, that as better the light of a given wavelength is emitted by a body, as better it is also absorbed by it. The validity of this, only on experimental way formulated Kirchhoff's law was theoretically derived only in the beginning of the 20th century by Einstein's introduction of transition probabilities and can be expressed by the following equation:

$$A_{ki} = (g_i 8\pi h v^3 / g_k c^3) B_{ki} \qquad (1)$$

Since the expressions in brackets are for a given transition constant, the coefficient of transition probability for the (spontaneous) emission $A$ is proportional to the coefficient of the transition probability for the (stimulated) absorption $B$ what confirms the Kirhoff's law.

Despite the presented knowledge concerning spectrochemical analysis and its great successes in astronomy by having described the atmosphere of the Sun and at the discovery of several new chemical elements (Cs – 1860 by Kirchhoff and Bunsen in mineral water from Kreuznach and Dürkheim; Rb – 1861 by Bunsen and Kirchhoff in lepidolite from Saxonia; Tl – 1861 by Crookes in residua after the production of sulfuric acid; In – 1863 by Reich and Richter in sphalerite from Freiberg; He – 1868 by Janssen and Lockyer in the Sun atmosphere and 1895 by Ramsay in cleveite and uraninite; Ga – 1875 by Lecoq de Boisbaudran in sphalerite from Pierrefitte; Ho – 1878 by Soret and Delafontaine in the earth from Swedish village Ytterby; Xe and Kr – 1898 by Ramsay and Travers in liquid air; Rn – 1900 by Debierne in radium compounds; Hf – 1922 by Coster and Hevesy in

zirconium containing minerals; and Re – 1925 by Noddack, Tacke and Berg in platinum ores) spectrochemical analysis remained for nearly one half century practically only as procedure for university investigations without any broader practical industrial application. This fact can be brought in connection with its insufficient quantification capacity caused by low spatial and temporal stability of used excitation sources. This situation is very clearly expressed in the 5$^{th}$ band of the Handbook of Spectroscopy the so called spectroscopic "bible" composed and published in 1910 by Heinrich Gustav Johannes Kayser (1853-1940): *"If I resume all the described investigations I come finally to the conclusion that quantitative spectroscopic analysis has been proved as non performable."*. How a non provident statement! Unfortunately, it was the First world war after which the first significant industrial application of spectral analysis was introduced by French scientist De Gramont (well known by older spectroscopists as constructor of the after him named electrode stand) who used spectroscopic analysis to classify steel or iron from captured German weapons before their reuse in iron mills. The origin of the proper creation of quantitative spectrochemical analysis was enabled practically first in 1933 by Wa. and We. Gerlachs' proposition do not to use directly the intensity values of analytical spectrum line which varies with the instability of the used light source and to replace it by its value related to the intensity of a suitably chosen reference spectral line of an element contained in the analyzed sample in relatively constant concentration. The relative intensity of so called homologous line pair is than practically independent on light source instability but mainly on the concentration of the analyte. This revolutionary change enabled to reach results loaded only by relatively low uncertainty (caused namely by the use of unconfortable and beside of it, complicated and slow photographic detection) enabling to obtain analytical results of acceptable precision and so to find a large application field in practically all cultural branches and this not only in science and technology (geology, chemistry, metallurgy, machinery, food production, health etc.) – as example can serve the statement that in metallurgy 90-95 % of all analyses are performed using spectroanalytical methods - but also in pure spiritual culture as e.g. in law (criminalogy), history (archeology), creative art (falsificates) and even in religion (analysis of Turin linen – supposed Jesus´ shroud).

A great merit in the development of spectrochemical analysis belongs also to the papal astronomical observatory *Specola Vaticana*, founded originally in Rome as Tower of winds by pope Gregor XIII. (Ugo Buoncompagni 1502-1585) for to prepare the new, after him named gregorian calendar introduced in 1582, as well as according to preserved legends to prove or to refuse the presence of human beings on the Moon or other sky objects in order to solve the problem if they also could have been redeemed by Jesus' death and resurrection or not. In this excellently equipped observatory mooved later to Castel Gandolfo near Rome, thanks to jesuite scientists of Austrian origin fathers Alois Gatterer S. J. (1886-1953) and his successors Joseph Junkes S. J. (1900-1984) and Ernst Salpater S. J. (1912-1976) eventually about the middle of the 20$^{th}$ century, also a world known spectroscopic laboratory was established. Several instrumental innovations and tables of spectrum lines lengths originated from this scientific group. To unforgettable Gatterer's merits belongs also the foundation of the first till now existing leading professional journal *Spectrochimica Acta* and the foundation of the most significant professional scientific meeting *Colloquium Spectroscopicum Internationale* which was later maintained by the so called triumvirat of famous spectroscopists Edmond Loeuil from France, Alexander Menzies from Great Britain and Heirich Kaiser from Germany.

It is not the aim of this contribution to enumerate all personalities who contributed to the recent significance of spectroscopy and to describe the whole further immense development of at least atomic spectrochemical procedures during and after the Second world war and namely in the last decades enabled by the use of simple, sensitive and fast detectors represented by photoelectric multipliers and solid state CCD or CID detectors, introduction of atomic absorption and fluorescence analysis, optical and mass spectrometry with inductively coupled plasma, X-ray fluorescence spectrometry etc. and to dwell upon the topic that all these successes have been supported by massive application of computerization. The recent state of art of spectrochemical analysis corresponds so to its position between automation and robotization with capacity to control full technological production systems.

**Conclusion**

The described origin and further extremely broad development, as well as application of spectroanalytical procedures shows their significance not only in science but also in the whole social being. Spectral analysis can be so thanks to its very good detection power, specificity in identification of elements, suitable reliability of results, speed and several other excellent metrological and economical parameters compared without exaggeration with the greatest cultural gains like the use of fire, domestication of animals, invention of writing, or creation of music. Let we therefore care with our greatest forces for a prosperous future development of spectral analysis and for its corresponding cultural acknowledgment!

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