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Historical Articles

Capillary Electrophoresis and its Basic Principles in Historical Retrospect

Part 1. The early decades of the "Long Nineteenth Century": The Voltaic pile, and the discovery of electrolysis, electrophoresis and electroosmosis

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Abstract. Here we set forth the first from a series of reports devoted to the history of capillary electrophoresis. In this opening part, we go more than two centuries back in time and revisit original discoveries of electrolysis, electrophoresis and electroosmosis. We emphasize the essential role of a brilliant invention of 1799 by Alessandro Volta, the Voltaic pile, basically the first battery delivering a constant-flow electricity, which has made all the scientific advances in the subsequent years and decades possible. We describe the experiments of William Nicholson and Anthony Carlisle revealing electrolytic decomposition of river water followed by enlightened investigations by Nicolas Gautherot, Ferdinand Frédéric Reuss and Robert Porrett that each independently and unaware of the works of the other uncovered the phenomena of electrophoresis and electroosmosis. We give not only a technical description and a chronological overview of the inventive experiments, but offer also some formidable details as well as circumstances surrounding some of the initial inventors and their observations. We conclude this time period, for which we coin the term "*1st epoch of electrophoresis*", with the same year 1914 as the astonishingly coincident period of the European history between the French revolution in 1789 and the begin of the First World War, termed the "*Long 19th Century*" by the British historian Eric Hobsbawm. We accentuate the surprising fact that over this entire cycle of 125 years no attempts were taken to utilize the findings and newly acquired knowledge to perform an electric driven separation of compounds from a mixture. In the field of electrophoresis and electroosmosis, it is rather the epoch of pure than of applied science.

Keywords: capillary electrophoresis, history, discovery, electroosmosis, electrolysis.

PREFACE

Electrophoresis is the motion of electrically charged particles, which are dispersed in a liquid, and which drift relative to the fluid under the influence of a spatially uniform electric field.[1] *Capillary Electrophoresis* is the version of electrophoresis in which the liquid is inserted into a narrow open tube.[2] The liquid dispersion can be a solution of ions, an emulsion or a sol of colloids or – in rarer cases – a suspension of coarse granular particles, a noteworthy differentiation, which is often ignored (colloids do not form solutions; please pay heed to footnote[3]). Notwithstanding that nowadays electrophoresis is nearly exclusively used as a separation method, the term *electrophoresis* classifies the electrically driven movement of charged particles of any size in liquids *in a general meaning.*

Electroosmosis (also named electro-endosmosis in the past), can be seen as the reverse phenomenon compared to electrophoresis. Hence, electroosmosis is the motion of a liquid around an electrically charged surface in response to an applied electric field.[4] The electrically charged surface could be an inner wall of a capillary, a membrane, a porous plug or an immobilized set of particles. Electroosmosis plays an important role in practical capillary electrophoresis, because its flow velocity adds to the velocity of the charged particles.

Review papers on capillary electrophoretic methods (e.g. refs. [4-8] and others) usually mention only briefly the historical background on which the electrically induced migration of ions or colloidal particles is based. Although we assume that in the majority of cases in practice the basic principles are known, we wish to lay out an investigatory tale of the development of the technique from a more general perspective including some noteworthy historic facts such as that – contrary to the widely accepted perception – electrophoresis in open narrow glass tubes with a few hundred micrometers inner diameter (today widely recognized as capillary electrophoresis) is not an invention from the 1960s. In fact, it was first systematically carried out nearly a century prior, *viz.* in the years 1860 and 1861 by T. Jürgensen[9] and by G. Quincke,[10] albeit not for separation purposes. Thus, we here put forward a retrospect of the history of (capillary) electrophoresis from a broader perspective.

In our opinion, this long period can be subdivided into three distinctive epochs:

In the *1st epoch* of electrophoresis (whereby *electrophoresis* was not named as such over the entire period[5]) the focus of the research was directed to the basic physical and chemical principles, hypothesis, theories and laws of the electrically-induced migration of charged particles in liquids, and of the electroosmotic movement of liquids. The decisive characteristic of this *1st epoch* is a lack of intent to use electrophoresis as a separation method. This epoch commenced by the discoveries of electrolysis, electrophoresis and electroosmosis. It was rendered possible by an invention of a tool that enabled these discoveries, *viz.* a source of constant-flow electric-

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[1] We do not always use the IUPAC recommendations (ref. [1] IUPAC, *Compendium of Chemical Terminology Gold Book*, Online version https://goldbook.iupac.org/ ed., **2014** [2] T. A. Maryutina, E. Y. Savonina, P. S. Fedotov, R. M. Smith, H. Siren, D. B. Hibbert, in *IUPAC Recommendations*, Pure Appl. Chem. ; 90(1): 181–231, **2018**.) because in some (rare) cases they are incomplete, ambiguous or out-of-date.)

[2] It is a matter of fact that no general definition exists for the inner diameter (i.d.) a narrow tube must possess to be considered as a capillary. In separation methods capillaries are open tubes with i.ds. of about 100 to 300 μm in capillary gas chromatography (GC), at the time of the replacement of the packed GC columns (which had i.ds. of 2 to 5 mm) by capillaries, so-called wide bore capillary columns with i.ds. of 540 μm were commercially offered. In modern instrumentation of capillary electrophoresis, the open tubes have i.ds. ranging from 25 to 100 μm, but also those with 5 μm i.d. are applied in zone electrophoresis and of 300 μm in isotachophoresis. The dimensions mentioned serve only as orientation for the reader.

[3] We use the following terminology for these liquid systems in the present paper:

The generic term for the different types of the particle-solvent systems is *dispersion*. In a *dispersion* the particles are distributed in a *continuous medium* (in electrophoresis the *continuous* medium is usually a liquid). Depending on the size of the particles, the following kinds of dispersions can be differentiated: (i) *solutions*, (ii) *emulsions* and *sols,* and (iii) *suspensions*.

ad (i) Small particles of molecular size (with typical radii in the range of several 10^{-10} m) *e.g.* stemming from electrolytes (either from solids like salts or from liquids like some pure low molecular weight saturated carboxylic acids) form a *homogeneous* mixture with the liquid, which is termed *solution*.

ad (ii) A *colloid*, synonymously termed *colloidal system* or *colloidal dispersion*, consists of a *heterogeneous* mixture of two phases, where the dispersed particles - *which are also named colloids* - are larger than small ions; their sizes range between about 10^{-9} and 10^{-6} m. Solid colloidal particles dispersed in liquids form *sols*, liquid colloidal particles form *emulsions.* Note that a colloidal system consists – in contrast to solutions - of two different phases, which are separated by an interface.

ad (iii) Particles which are larger than colloids form *suspensions as heterogeneous dispersions* in the liquid. Other than solutions and colloids, the particles sediment during long-standing periods. A special case are *gels* in which liquids are dispersed in solids.

[4] Other electrokinetic phenomena are the streaming potential and the streaming current, the sedimentation or centrifugation potential gradient, the colloid vibration potential, and the electrokinetic sonic amplitude. They do not play a role in the present topic. Readers are referred for details to ref. [3] J. Lyklema, *Fundamentals of Interface and Colloid Science. Vol. II: Solid-Liquid Interfaces, Vol. 2*, Academic Press, London, San Diego, **1995**.

[5] As typical examples we mention that F. Kohlrausch, who was one of the leading scientist in the area of ion migration, entitled his paper from 1893 "Über die Geschwindigkeit elektrolytischer Ionen" (*On the velocity of electrolytic ions*), ref. [11] F. Kohlrausch, *Ann. Phys. Chem.* **1893**, *50*, 385-408., and that from 1897 which served as base for the understanding of the different electrophoretic separation methods "*Ueber Concentrations-Verschiebungen durch Electrolyse im Inneren von Lösungen und Lösungsgemischen*" (*On concentration shifts due to electrolysis inside solutions and mixtures of solutions*"), ref. [12] F. Kohlrausch, *Ann. Phys. Chem.* **1897**, *Neue Folge Band 62*, 209-239. Both papers deal with ion migration, not with electrolytic processes.

ity by Alessandro Volta in 1799, the Voltaic pile, which transformed chemical into electric energy. However, we let this *1st epoch* begin even earlier, that is to say by the initiation of Volta´s ideas of a new kind of electricity which contrasted the misinterpretation of the well-known frog experiments by Luigi Galvani in the 1780s.

During the 125 years following Galvani´s experiments and the invention of Volta´s pile electrophoresis was applied solely to study the physical and chemical properties of pure compounds. Surprisingly, although all principles that govern the migration of ions and of dispersed colloidal particles in free solutions[6] were already progressively known, no attempts were made to apply them to separate constituents of mixtures. This *1st epoch* lasted until the midst of 1910 with the first intentional use of electrophoresis to perform separations in free solutions and it is the time period covered by the first series of our historical expeditions.

Due to his reading of the political works of the prominent British historian Eric J. E. Hobsbawm,[7] one of the present authors (E.K.) ascertained the remarkable coincidence of the duration of this *1st epoch* with an era referred to as the "*Long 19th Century*" in political sciences, specifically the time between the French revolution in 1789 and the begin of the First World War in 1914. The term *Long 19th Century* was introduced as a kind of a clamp for the first three volumes of Hobsbawn's tetralogy on the history of the 19th and of the 20th century.[13-15] Due to this astonishing temporal co-occurrence we have adopted the term *Long 19th Century* for the *1st epoch* of electrophoresis, which is the topic of the first series of our retrospect.

The *2nd epoch* of the history of (capillary) electrophoresis we let begin with its first intended utilization as separation method in the midst of 1910, and this period lasted till the 1990s. For the *2nd epoch* of electrophoresis we adopt the name, the "*Short 20th Century*", from the fourth volume of Eric Hobsbawn's tetralogy entitled *The Age of Extremes: The Short Twentieth Century, 1914–1991.*[16] In this book, the *Short 20th Century* was defined as the time period between the begin of the First World War in 1914 and the collapse of the USSR in 1991. During this time various electrophoretic methods were developed for the separation of ionic and colloidal particles. A notable highlight was the spectacular separation of serum globulins by Arne Tiselius in 1937 (awarded the Nobel Prize in 1948) by using the moving boundary method in free solution (which is one of the variants of electrophoresis). Nota bene that the separation followed the principles of the "*beharrliche Funktion*", the *regulating function*, derived by Friedrich Kohlrausch already in the previous *1st epoch* (*viz.* in 1897).[12]

It is to mention that during the first part of this *2nd epoch* most of the electrophoretic separations were not carried out in free solutions, they applied supporting or separating materials like paper, gels, etc. In contrast, our main interest is directed on electrophoresis in the capillary format in free solution, which was introduced in the 1960s. This method obeys the laws of the traditional electrophoresis in free solution, those which were derived during the *Long 19th Century*, and were refined at the begin of the *Short 20th Century* (e.g. by the concept of the chemical activity).

In the 1960s several variants of capillary electrophoretic techniques were established, mainly by the pioneering work of Frans Everaerts and his coworkers in Eindhoven with isotachophoresis (see e.g. ref. [17]), and by Stellan Hjertén in Uppsala with zone electrophoresis (see e.g. ref. [18]). These methods, (interestingly both were suggested by Nobel laureates, A. J. P. Martin and Arne Tiselius, respectively) were performed in open narrow-bore tubes with inner diameters down to ca. 200 μm. At this time, isotachophoresis (persistently called *displacement electrophoresis* by Hjertén), became the dominant variant, while capillary electrophoresis itself played only a niche role compared to well-established chromatography and gel-based electrophoresis.

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[6] We are fully aware of the fact that only ions can be dissolved and exist then in free solution, but colloidal particles are forming emulsions or sols, not solutions. However, we further use for the sake of convenience the attribution *free solution* also to colloidal particles.

[7] Eric John Ernest Hobsbawm [1917 (Alexandria, Egypt) - 2012 (London)] was a British historian with marxist orientation. The family of his father, named Obstbaum (verbatim in English translation "fruit tree"), had migrated from Austria to Great Britain and modified the name to Hobsbawm. The father got a position in the Sultanate Egypt, which was a British protectorate at that time. His mother came from a wealthy Viennese family. After the First World War, the family went back to Vienna, where they lost their assets due to the gigantic inflation at that time. After the death of his parents (the father died in 1929, the mother in 1931) relatives took Hobsbawm to Berlin, where he came in contact with the German Communist Party. In 1933, the family went to London. For the following years Hobsbawm received a stipend for Cambridge, where he became member of Communist Party of Great Britain, what he remained livelong. In 1947, Hobsbawm became lecturer at an evening school at London University, the Birkbeck College. During this time, he published Jazz-critiques in *New Statesman* under the pseudonym Francis Newton. After publication of his tetralogy between 1962 and 1987 (ref. [13] E. J. E. Hobsbawm, *The Age of Revolution: Europe: 1789–1848*. Ref. [14] E. J. E. Hobsbawm, *The Age of Capital: 1848–1875*. Ref. [15] E. J. E. Hobsbawm, *The Age of Empire: 1875–1914*. Ref. [16] E. J. E. Hobsbawm, *The Age of Extremes: The Short Twentieth Century, 1914–1991*) about the history of the 19th and the 20th century he became known worldwide. For the time period between 1789 and 1914, described in the first three volumes of his tetralogy, the term the *Long 19th Century* was coined, that described in the fourth volume over the years between 1914 and 1991 was termed the *Short 20th Century*. Not until 1971 he was appointed professor in London, where he died at the age of 95.

The *2nd epoch* was concluded in the late 1980s with the advent of a new capillary material – amorphous quartz, named fused silica – which has led to a sudden increase of interest in the separation methods community. The favorable mechanical, optical and surface properties of this material, which has extensively been exploited in gas chromatography, facilitating an enormous separation capability and a highly sensitive detection of extremely low quantities of analytes, prompted the commercial availability of a number of different user-friendly instruments. Consequently, capillary electrophoresis, especially the *zone electrophoresis* version, became a member of a family of the high performance separation methods

The *Short 20th Century*, lasting only 75 years from midst 1910s to about 1990, was followed by that we are consequently terming the *3rd epoch* of electrophoresis, which brought an outstandingly large number of innovative experimental and instrumental approaches as well as novel applications. Coupling to mass spectrometry has brought a new dynamic to capillary zone electrophoresis. Perhaps the outmost notable achievement was a transfer of the classic size-based separation of DNA fragments from slab-gel electrophoresis into capillary electrophoresis mainly enabled by the introduction of linear entangled polymers as replaceable sieving matrices. This progress enabled, to mention only one well-known example, the execution of the Human Genome Project, which started 1990 and completed officially 2003 with the determination of the entire DNA sequence of the euchromatic human genome.

In the present *3rd epoch*, capillary electrophoresis is an indispensable tool in nearly all scientific disciplines, in life sciences for instance in genomics, proteomics and metabolomics. Since current research is the topic of this *3rd epoch*, we will not include it in our historical retrospect. This time is rather the theme of a topical, not of a historical review.

Following this brief overview, we will now return back to the dawn of the discoveries of the electric phenomena in the early decades of the *Long 19th Century*, to the period between the late 1780s and the midst 1810s.

AT THE TURN TO THE *LONG 19TH CENTURY*

Until the end of the 18th century the sources of electricity were electrostatic generators or electrostatic machines. These devices transformed mechanical work into electrical energy by a process of generation of charge by friction and induction. One such a device was invented in the 1760s by the Swedish physicist Johan Carl Wilcke (Wilke in his papers written in German language)[19-21] and re-invented and improved by Alessandro Volta in 1775 who named it *elettroforo perpetuo*. It was a simple generator of static electricity by induction, which became very popular as *electrophore* or *electrophorus*.[8]

A drawing of an *electrophore* is shown in Figure 1. It consists of two plates.[9] The bottom plate, the *cake* or *sole*, is a dielectric, *i.e.* an electrically non-conductive material. A detailed instruction for the preparation of an electrophorus in a book from 1814[23] recommends a resinous "*cake*" of about half an inch thickness, formed by melting equal parts of resin, shellac and Venice turpentine[10] together. The upper part (the "*cover*") is a metal plate with an insulated handle, comparable with the plate of a capacitor. Electricity is generated by electrostatic induction (see footnote 11).

The generated electricity could be stored e.g. at a special cylindrical capacitor, the *Leyden jar*. Though this

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[8] We have chosen this device, because it demonstrates the principle of the generation of static energy in a very simple form. In addition, we accentuate that the term *electrophore* points to the little known fact that a word combined from Greek ήλεκτρον ('*elektron*'), and φέρω ('*phero*'), freely translated as "*the bearer of electricity*", was in use already in the 18th century. It was not a new term when it was introduced at the begin of the *2nd epoch* of electrophoresis for the method under discussion in the present paper.

[9] An early description of this popular device is given e.g. in Chapter IV, p. 380.389, from ref. [22] T. Cavallo, *A Complete Treatise of Electricity in Theory and Practice with Original Experiments*, Edward and Charles Dilly, London, **1777** or later in 1814 on p. 121-122 of ref. [23] G. J. Singer, *Elements of Electricity and Electro-chemistry*, London, **1814**. In this book, a large number of practical experiments are describes. A further description is given in the section "*L´Électrophore*" in *Chapitre IX. Des Electricités dissimulées*. in Vol. 1, pp. 571-575, of Jean-Baptiste Biot´s textbook of experimental physics from 1821 (1st ed. in 1817, (ref. [24] J.-B. Biot, *Précis élémentaire de physique expérimentale. Tome I, Vol. 1*, 2nd ed., Deterville Paris, **1821**.)

[10] Venice turpentine is a highly viscous oleoresin, a mixture of bicyclic diterpenoid compounds, mainly with carboxylic and alcoholic functional groups. It is collected from the exudate of the European larch in Tyrol, Austria. It must not be confused with oil of turpentine, which is a mixture of liquid monoterpenes.

[11] For the generation of electricity, the upper surface of the earthed bottom resin plate becomes negatively charged by rubbing, e.g. by a piece of dry fur (cat´s skin is the best, according to ref. [23]), or a piece of wool. Then, the metal plate is placed on the "*cake*", and becomes positively charged by induction at the surface directed towards the cake, and negatively at the opposite surface of the metal. The plate is taken off from the cake, then the upper, opposite surface is touched with a finger, causing the transfer of the negative charge to ground. At the metal plate only the positive charge formed by induction remains. It can then be, for example, transferred to a Leyden jar. This operation can be repeated many times without the need to rub the resin again, and was therefore termed by Volta *elettroforo perpetuo* (*perpetual electrophorus*).

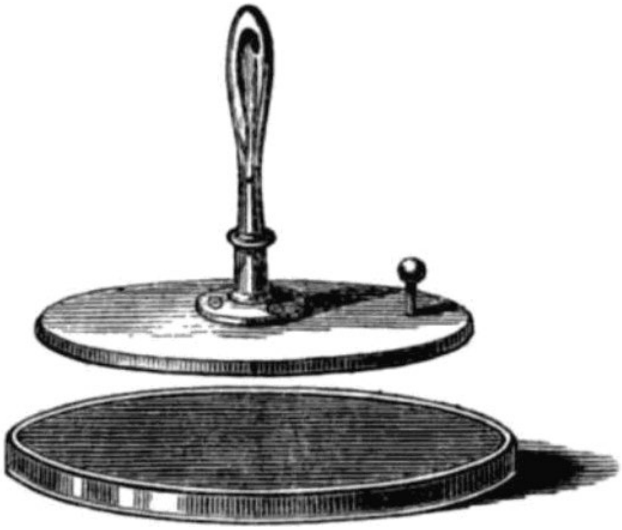

Figure 1. Drawing of an *electrophore* or *electrophorus* (Volta termed it *elettroforo perpetuo),* a device for the generation of static electricity by induction. For explanation, see footnote 11. Taken from ref. [25].

capacitor was able to deliver large electric potentials,[12,13] it's capacity to store static electric energy was low, which required frequent recharging for use over longer period of time. The capacity could be increased by connecting several jars in parallel, forming a *Leyden battery* in this way.[14] However, the need for recharging remained and, further to its disadvantage, the discharge current did not remain constant.

A new aspect for the generation of electricity was unintentionally opened up by Luigi Galvani´s false conclusions of his experimental results. Galvani,[15] professor of anatomy in Bologna, investigated since early 1780s the effect of electricity on animals. Galvani´s findings, which he misinterpreted, were the prelude for the invention of a revolutionary new source of electricity by Alessandro Volta. The story began with an observation of one of Galvani´s students, who touched with the tip of a scalpel a lumbar nerve of a dead skinned frog which was placed nearby an electrostatic machine. This accidental contact caused a convulsive twitching of the frog´s legs as if alive. Galvani, who assumed a context of this contraction with electricity, commenced in 1789 a series of experiments by which he noticed that the muscles of the frog´s legs were contracted even in the absence of an electrostatic machine. They also twitched when they were connected by contacts made of two different metals (e.g. of copper and iron).[16] Galvani postulated that the source of this contraction was a new kind of electricity, which he termed *animal electricity.* He believed that this new energy was intrinsic to the body of the dead frog, and hypothesized that the frog´s brain produced electricity, and its body acted as a kind of electric condenser. He further assumed that the nerves are the conductors which transmit the electricity to the muscles. Galvani published his findings in 1791 in "*De viribus electricitatis in motu musculari commentaries*" ("*Commentary on the Effects of Electricity on Muscular Motion*"),[28] which attracted extraordinary attention by his scientific colleagues, amongst them also by Alessandro Volta.[17]

THE VOLTAIC PILE

Volta was highly experienced in the field of static electricity, and was initially convinced by the existence of the animal electricity, but since summer 1892 he began to doubt Galvani´s hypothesis of animal electricity. Volta, in contrast, supposed, that the source was the contact electricity originating from the metallic wires in connection with the interposed body fluid of the frog as a conducting medium. He executed experiments with different metals and was able to measure even very low quantities of electricity when the metals were brought into mutual contact.[18] [31]

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[12] In the literature, *voltage* has normally been used to describe the *electric potential difference*. According to IUPAC "*…this term is discouraged, and the term applied potential or (electric) potential should be used instead for non-periodic signals…*" (PAC, 1985, *57*, 1491 *(Recommended terms, symbols, and definitions for electroanalytical chemistry (Recommendations 1985)),* p. 1505). In order to avoid confusion, we prefer to use the term (*electric*) *potential difference* if appropriate.

[13] With replica of historical Leyden jars potential differences of several ten thousand Volt were obtained.

[14] We consider *n* capacitors, *i*, connected in parallel, and use the symbols *U* for potential, *Q* for charge, and *C* for capacity. Then $U_{\mathrm{tot}} = U_{\mathrm{i}}$; $Q_{\mathrm{tot}} = \Sigma Q_{\mathrm{i}}$; $C_{\mathrm{tot}} = \Sigma C_{\mathrm{i}}$. This connection in parallel is applied to increase the capacity of the Leyden battery. Upon discharging of the capacitor, the discharge current, *I*, decreases exponentially with time, *t*, according to $I(t)=-I_0\, e^{-t/\mathrm{t}}$; *t* is the time constant of the discharge process.

[15] Luigi Aloisio Galvani [(1737) Bologna, Papal States, at present Italy - 1798], (in Latin *Aloysius Galvanus*) was an anatomist, physician, physicist, physiologist and biologist.

[16] Very detailed descriptions of Galvani´s observations are given e.g. in ref. [26] E. Du Bois-Reymond, *Untersuchungen über thierische Elektricität, Vol. 1*, G. Reimer, Berlin **1848**., and in ref. [27] O. E. J. Seyffer, *Geschichtliche Darstellung des Galvanismus*, J.G. Cotta, Stuttgart und Tübingen, **1848**.

[17] Alessandro Giuseppe Antonio Anastasio Volta, [1745 (Como, at present northern Italy) - 1827], since 1810 Count Volta; since 1774 professor of physics at the Royal School in Como, and professor in natural philosophy, and chair in experimental physics at the University of Pavia since 1819.

[18] The measurement of very low quantities of electricity was possible by a device which combined a condenser – which Volta constructed and built – with an electrometer created by Tiberius Cavallo (described in his book, ref. [22] T. Cavallo, *A Complete Treatise of Electricity in Theory and Practice with Original Experiments*, Edward and Charles Dilly, Lon-

He also found that the quantity of the generated electricity was higher when the two metals were separated by a third, non-metallic conductor, for example by a 2nd class conductor like a piece of paper soaked with salt solution.[32, 33] Thus, Volta argued that the nerves in Galvani´s experiments were stimulated by the electricity delivered by the communicating metals,[34] not by animal tissues, and believed in what he coined *metallic electricity* instead of Galvani´s *animal electricity.*

The debate between the two scientists ultimately led to the refusal of Galvani´s idea of an animal electricity (which was, with Volta´s generous agreement, further named *galvanic electricity*, and its topic *galvanism*; for details, see e.g. ref. [35]). The seminal result of Volta´s investigations of his metallic electricity was the creation of an electric element, which transformed chemical into electric energy.[19]

In contrast to the Leyden jar, Volta´s device enabled the generation of a continuous and constant-flow electricity. In 1800 Volta described the battery, a stack of assembled electrochemical elements later named *Voltaic pile*, in a detailed paper titled "*On the Electricity excited by the mere Contact of conducting Substances of different Kinds*".[37] He sent the description of the pile as a letter dated March 20, 1800 to the President of the Royal Society, Sir Joseph Banks. The letter was read June 26, 1800 befor the Royal Society in London.[38] Following we include the verbatim reproduction of the first two paragraphs from Volta´s letter to Banks with its exemplary clear description of the battery, and illustrate this explanation in Figure 2.

> …In prosecuting his experiments on the electricity produced by the mere contact of different metals, or of other conducting bodies, the learned Professor was gradually led to the construction of an apparatus, which in its effects seems to bear a great resemblance to the Leyden phial, or rather to an electric battery weakly charged; but has moreover the singular property of acting without intermission, or rather of re-charging itself continually and spontaneously without any sensible diminution or perceptible intervals in its operations. The object of the present paper is to describe this apparatus, with the variety of constructions it admits of, and to relate the principal effects it is capable of producing on our senses.
>
> It consists of a long series of an alternate succession of three conducting substances, either copper, tin and water; or, what is much preferable, silver, zinc, and a solution of any neutral or alkaline salt. The mode of combining these substances consists in placing horizontally, first, a plate or disk of silver (half-a-crown, for instance,) next a plate of zinc of the same dimensions; and, lastly, a similar piece of a spongy matter, such as pasteboard or leather, fully impregnated with the saline solution. This set of threefold layers is to be repeated thirty or forty times, forming thus what the author calls his columnar machine. It is to be observed, that the metals must always be in the same order, that is, if the silver is the lowermost in the first pair of metallic plates, it is to be so in all the successive ones, but that the effects will be the same if this order be inverted in all the pairs. As the fluid, either water or the saline solution, and not the spongy layer impregnated with it, is the substance that contributes to the effect, it follows that as soon as these layers are dry, no effect will be produced."

As depicted in Figure 2 any number of elements can be combined in order to increase the total electric potential of the pile. In his letter Volta described that each element consists of a pair of discs made from three materials, *viz.* from two different metals and a layer of a matter wetted with water or saline solution; the elements can be stapled about each other.[20] At the uppermost and the lowermost disc, respectively, metal wires are attached, and each of these elements contributes additively to the electric potential of the pile by its individual potential which depends on the kind of the metals.[21] Effects of

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don, **1777**. Volta´s device was presented for the Royal Society in London, read March 14, 1782, entitled "*Del modo di render sensibilissima la piu debole Elettricità sia Naturale, sia Artificiale*" (ref. [29] A. Volta, *Phil. Trans. Roy. Soc. (London)* **1782**, *72*, 237-280. ("*Of the Method of rendering very sensible the weakest Natural or Artificial Electricity*") and ref. [30] A. Volta, *Phil. Trans. Roy. Soc. London. Part I* **1782**, *72*, 453 (vii-xxviii). This sensitive device was also essential for Volta´s research on his pile.

[19] Sir Humphry Davy, [1778 (Penzance, Cornwall, England) - 1829], teacher and mentor of Michael Faraday, said Volta's work was "*an alarm bell to experimenters all over Europe*" (see *e.g.* ref. [36] C. Russell, in *Chemistry World, Vol. 1 August 2003*, Royal Society of Chemistry, **2003**.).

[20] In each single Volta element in Figure 2 zinc is oxidized to Zn^{2+}, and releases 2 electrons. For the electrochemical reduction at the silver electrode several reactions are possible. If the silver plate is covered by a layer of silver oxide or silver salt (as it is when e.g. used half-a-crown coins are applied, as mentioned in Volta´s letter), Ag^+ can be directly reduced. In absence of silver ions, e.g. when the plate is polished, oxygen from air or hydrogen ions from the impregnation solution can be reduced.

[21] In the Voltaic pile the elements (also named cells) are connected in series, i.e. the plus pole of the one element is connected with the minus pole of the adjacent element. All elements are flown through by the same current, which has the disadvantage that it is determined by the element with the lowest current. In the worst case the potential fails if one element is defective. The total electric potential difference of the series of elements of the battery is equal to the sum of the potentials differences of its single elements. The potential difference of an element made for instance from zinc and copper is about 1.1 Volt. Thus, in a staple of say 10 elements the applied potential is about 11 Volt between the two extreme discs.

When the elements are connected in parallel (which is not the case in the Voltaic pile), i.e. when the plus pole of the one element is connected with the plus pole of the adjacent one, and the minus pole with the minus pole, the load capacity of the battery (in A.h, Ampere hours) is the sum of the load capacities of the single elements. The total electric

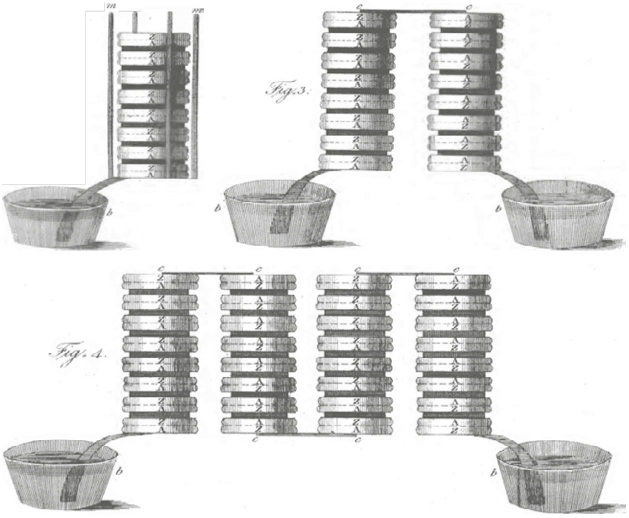

Figure 2. Drawing of Volta´s piles combined from 8, 16 and 32 elements, respectively, consisting of pairs of zinc (Z) and silver (A) discs. In these piles, the elements or cells are formed by a pair made from two discs of different metals which are in direct contact, in this Figure of silver, A, and zinc, Z, communicating with the next pair by an interposed spongy matter (e.g. a piece of cloth, leather, or pasteboard) moistened with a salt solution. The elements are stapled one upon the other, here with a silver disc as the lowermost, and a zinc disc as the uppermost one. Taken from ref. [37].

electricity on solutions could be investigated by immersing the wires` tips of the pile into the liquid, where they act as the electric poles.[22]

At last, we want to contrast Volta's story of his triumphant scientific successes – among many other honors he was made a Count in 1810 by Napoleon after the conquest of Italy – with a largely unknown and rather tragic-comic story, which is a matter of the metallic electricity Volta discovered. As early as in May 1793 John Ribison, [1739-1805], a British professor of natural philosophy at the Edinburgh University (he was physicist and mathematician) reported a peculiar experiment in a letter[39] sent to Alexander Fowler, the editor of "*Experiments and Observations relative to the Influence Lately Discovered by M. Galvani, and commonly called Animal Electricity*",[40] (translated into German in ref. [41]). The experiment was carried out by Ribison`s son, who brought a piece of silver and a piece of zinc in contact with his tongue and felt a strong stimulus, similar to a taste. Ribison repeated this experiment and obtained the same result. He was aware about some curious discoveries which had been made in Italy some time ago, but he had no further knowledge of what was going on in the recent years.

We describe here only some of the experiments which he reported in the letter. In one particular experiment he felt the same irritation at the tongue as already mentioned above when he placed a piece of zinc, in contact with a piece of silver at any other part of the mouth, the nose, the ear, the urethra or the anus. Also he applied a piece of zinc onto a wound of a toe, and a piece of silver to the tongue, and each time when he brought the metals in contact he felt a painful irritation at the wound where zinc was placed. Next, Ribison applied a rod of zinc and one of silver to the roof of the mouth. Upon connecting the ends of the rods, he felt a painful, convulsive pruritus, together with a bright refulgence in the eyes. Finally, Ribison made a number of pieces of zinc of the size of a shilling-coin and formed a roll with an equal number of silver shillings. He observed under certain conditions an intensified irritation at the tongue, which was increased when the tongue touched all pieces of the metals at the side of the roll, effects which sourced from contact electricity.

Ribison´s report ended with his regret that he was not able to continue his experiments due to his indisposition. One might speculate that under more favorable circumstances he possibly invented an electric battery even few years prior to Volta.

THE DECOMPOSITION OF WATER BY ELECTRICITY: THE DISCOVERY OF ELECTROLYSIS

Volta sent his above mentioned letter in two separate parts to Sir Joseph Banks in London. After receipt of the first part of this letter, Banks has shown its first pages to Antony Carlisle.[23] It was already known that electricity can be sensed as electric "shocks", e.g. when electrostatic batteries were getting in touch with wetted hands or with the tongue. Based on the description in the letter, Carlisle assembled a pile, and – together with his friend William Nicholson[24] – repeated on April, 30 several experiments which were described in Volta´s letter (a

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potential difference of the battery is equal to the electric potential difference of the single elements in case of their connection in parallel.

[22] In the contemporary literature, the terms electrode and electrolyze were unknown; they were proposed about three decades later by M. Faraday. The term pole was used in analogy to the poles of a magnet.

[23] Anthony Carlisle [1768 (Stillington, England) – 1840], an English surgeon, was professor of anatomy of the Royal Society from 1808 to 1824. As a matter of curio we mention that Carlisle is probably the anonymous author of the gothic novel *The Horrors of Oakendale Abbey*, published in 1797 and previously attributed to "Mrs. Carver".

[24] William Nicholson [1753 (London) – 1815], an English chemist, founded the *Journal of Natural Philosophy, Chemistry and the Arts* in 1797 (known as *Nicholson's Journal*). It was the first English monthly scientific journal.

graphical interpretation of their experiments is shown in Figure 3). Nicholson subsequently reported[42]

> This pile gave us the shock as before described, and a very acute sensation wherever the skin was broken. Our first research was directed to ascertain that the shock we felt was really an electrical phenomenon. For this purpose the pile was placed upon Bennett's gold leaf electrometer, and a wire was then made to communicate from the top of the pile to the metallic stand or foot of the instrument. … In all these experiments it was observed, that the action of the instrument was freely transmitted through the usual conductors of electricity, but stopped by glass and other nonconductors. Very early in this course, the contacts being made sure by placing a drop of water upon the upper plate, Mr. Carlisle observed a disengagement of gas round the touching wire. This gas, though very minute in quantity, evidently seemed to me to have the smell afforded by hydrogen when the wire of communication was steel.

Being interested whether or not this release occurs also when the wires were placed separated from each other, in a series of experiments Carlisle and Nicholson filled river water into a glass tube, and plunged the two wires in a distance of several centimeters from each other into the water. Upon closing the electric circuit, an effect which surprised the experimenters was observed, *viz.* that at one of the wires a fine stream of bubbles of oxygen, at the other wire bubbles of hydrogen evolved.[25] After testing wires made of several different metals, the most distinct result was obtained with platinum or gold.

It was obvious that the evolved gases must originate from the water, but the question raised how the gaseous hydrogen or oxygen could be invisibly transported through the liquid water to the opposite pole when they were formed – as initially assumed – at one and the same pole and from the same individual water molecule (for more details of this anecdote the readers are recommended to ref. [36]).

Since it was evident that the two gases are products of the disintegration of water, Carlisle and Nicholson observed for the first time an electrochemical decomposition, which was later – as proposed by Michael Faraday – termed *electrolysis*. Nicholson published the results[26] - prior to the publication of Volta's letter[37] – in a paper entitled *"Account of the new Electrical or Galvanic Appa-*

Figure 3. An illustration of an experiment of electrolysis by William Nicholson and Anthony Carlisle on May 2, 1800, by decomposing water by electricity of a Voltaic pile. Taken from ref. [45], "*La Pile de Volta*", Chapter III, p. 629, Fig. 324.

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[25] It has to be mentioned that the decomposition of water by electricity, albeit not by an electrochemical reaction, was already carried out prior to the invention of the Voltaic pile, viz. by electric machines. George Pearson reported in 1797 the experiments made by the Dutch chemists Adriaan Paets van Troostwyk and J. R. Diemann, assisted by John Cuthbertson (see ref. [43] G. Pearson, *Phil. Trans. Roy. Soc. (London)* **1797**, *LXXXVII*, 142-157.; and ref. [44] G. Pearson, *Journ. Nat. Philos Chem. & Arts* **1797**, *1*, 241-246.). Cuthbertson was a highly qualified maker of scientific instruments and Fellow of the Philosophical Society of Holland and Utrecht. In the cumbersome and laborious experiments electric sparks generated by a Leyden battery were induced in succession in liquid water, which was decomposed into gaseous oxygen and hydrogen in measures of one to two. After collecting a sufficiently large quantity of the liberated gases, a spark was sent through them, causing their inflammation and the reconversion into liquid water.

[26] The first public report about these experiments appeared in the "*Morning Chronicle*", a London newspaper, on May 30, 1800. The authors found this information in Otto Ernst Julius Seyffer´s "*Geschichtliche Darstellung des Galvanismus*", ("*Historical presentation of the galvanism*"), published in 1848, ref. [27] O. E. J. Seyffer, *Geschichtliche Darstellung des Galvanismus*, J.G. Cotta, Stuttgart und Tübingen, **1848**. The book contains about 640 pages and describes in detail the history of the galvanism, from its first observation by J.G. Sulzer as soon as in in 1760 in Berlin, and Galvani in 1790, till 1845, with addition of some sources till 1847. It describes the contributions of about 600 authors (including the source of their publications), it circumstantiates detailed experimental set-ups, procedures and results in many contributions, it describes the reception of the results, controversial discussions between the authors, and puts them into the historical context. This is, in the opinion of the authors, an enormous achievement of Seyffer, considering the difficulty to get access at that time to the large number of different German, English, French, Italian and Russian journals.

ratus of Sig. ALEX. VOLTA, and Experiments performed with the same" in 1801 (in the July 1800 issue) in *Journal of Natural Philosophy, Chemistry, and the Arts.*[42] It is to be stated that the observations which were made by Nicholson and Carlisle in April and May 1800 introduced electrochemistry as a new scientific discipline.

The spectacular invention of Volta (and the effect of electricity on the decomposition of water) was rapidly communicated by the scientist across Europe, and provoked an eminent impulse for research in this novel discipline. Although the fact of the decomposition of water at the poles was corroborated by the formation of the gas bubbles, the transport of the electricity[27] through the solution remained completely unintelligible.

In the course of the various experiments which were executed by numerous researchers in Europe other phenomena that could occur between the two poles of Volta´s pile were discovered. The observation of these phenomena was facilitated because they could directly be followed visually. It was the migration of dispersed coarse granular particles, and – under certain conditions – the electrically induced movement of the liquid. The former phenomenon is now known as *electrophoresis*, the latter as *electroosmosis*.[28]

THE DISCOVERY OF ELECTROPHORESIS AND ELECTROOSMOSIS BY N. GAUTHEROT, F.F. VON REUSS AND R. PORRETT

Until the midst of the 19th century, Robert Porrett[29] was accounted as the discoverer of electroosmosis. This attribution was based on a paper which he published in 1816, entitled "*Curious galvanic experiments*"[46] (in 1820 in German).[47] In one of the described experiments, Porrett divided a glass jar by a bladder, obtaining two separated chambers in this way. When he filled one chamber with water the other chamber remained dry even when left for several hours as the water did not penetrate the bladder. Next, Porrett put a few drops of water into the empty chamber, just covering its bottom. Then he used a Voltaic pile connecting the positive pole to the water-filled chamber and the negative pole to the chamber with wet. Porrett then observed that water was transferred from the water full chamber through the bladder divider into the nearly empty chamber, resulting, within half an hour after completion of the electric circuit, in equal water levels in both chambers. This transport process further continued, raising the level in the negative chamber ¾ of an inch above the level of the positive chamber. Without having an explanation for this phenomenon Porrett named it *electro-filtration*. With our hindsight it is evident that the water transport observed by Porrett was by electroosmosis due to the electric double layer formed in the pores of the bladder.

The discovery of electroosmosis has been attributed to Porrett until the midst of the 19th century, when Otto Ernst Julius Seyffer referred to two experiments by Ferdinand Frédéric Reuss (Ferdinand Friedrich von Reuß)[30] published about one decade prior to Porrett, but which up to that moment were nearly unnoticed so far by the majority of the scientific community. In his book from 1848 Seyffer identified Reuss as the discoverer of electrokinetic phenomena.[27]

As reminded by Seyffer, Reuss described the execution of two experiments in publications which appeared in a Russian journal in 1809 (in French)[48] and in 1821 (in Latin).[49] The first publication was entitled "*Sur un nouvel effet de l'électricité galvanique*", the paper from 1821 "*Electricitatis Voltanae potestatem hydragogam tanquam novam vim motricem, a se detectam, denuo proposuit ejusque in naturae operibus partes investigare tentavit*" (Reuss was well-known for his chemistry lectures at the University held in Latin). In the first experiment Reuss packed quartz sand between two platinum wires (*a* and *b* in Fig. 4, top drawing) positioned as electric poles at the bottom of a V-shaped quartz tube. The tube was filled with degassed water, and the platinum wires were connected to a Voltaic pile. After closing the electric circuit, Reuss observed the already known decomposition of water under formation of gaseous oxygen and hydrogen at the poles.

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[27] At that time and later the flow of the electric current was named *the transport of electricity*. However, transported are the charges, either by the electrons in 1st class conductors like metals, or by ions or other charged particles in 2nd class conductors, e.g. in electrolyte solutions or in melted salts. For historical reasons, we temporarily also use the term *transport of electricity.*

[28] It is pointed out that the terms *electrode*, *electrolysis*, *electrophoresis*, *electroosmosis*, to name a few, were not known at that time. The first use of the term electro-endosmosis or electroosmosis was initiated in the 1830s, the term electrophoresis one century later**.** We use these terms (ahistorical) in the present paper when it serves for its better readability.

[29] Robert Porrett Jr. [1783 (London) – 1868] was chief administrator of the armory of London Tower by profession. He was member of the Society of Antiquaries and Fellow of the Chemical Society. Interested in chemistry and physics, he obtained thiocyanic acid from Prussian blue (Berlin, Parisian, Paris or Turnbull's blue, Iron(II,III) hexacyanoferrate(II,III)) upon reaction with potassium sulfide. and examined, amongst others, the chemistry of compounds containing iron and cyanide.

[30] Ferdinand Friedrich von Reuß [1788-1852] was born in Tübingen, Germany, where he studied medicine. He finished his studies in Göttingen as Dr. med. et chir. and became college lecturer for general medical chemistry in 1801. He became known for his investigations of the horse lymph, which was probably the cause for the assignment to a professorship at the Imperial University Moscow in 1808. In addition, he was professor for chemistry and pharmacography at the Imperial medico-chirurgical Academy from 1817 to 1839.

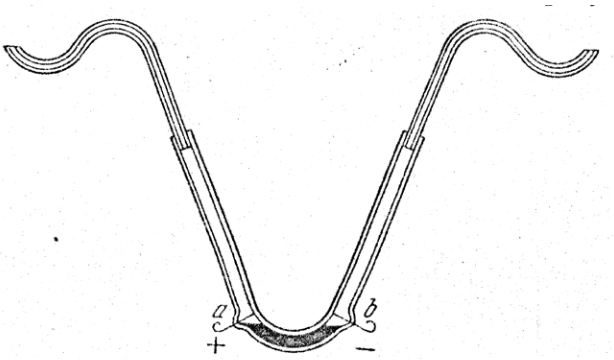

Figure 4. V-shaped quartz tube device used by Reuss in his first experiment on electroosmosis. The dimension of the tube was "3 *lignes de diamètre et de 7 pouces de lorgueur"*, i.e. 3x2.26 mm in diameter and 7x2.706 cm in length. The stippled portion is quartz powder. *a* and *b* are the wires of the + and the – pole, respectively. Reproduced from Reuss, ref. [48].

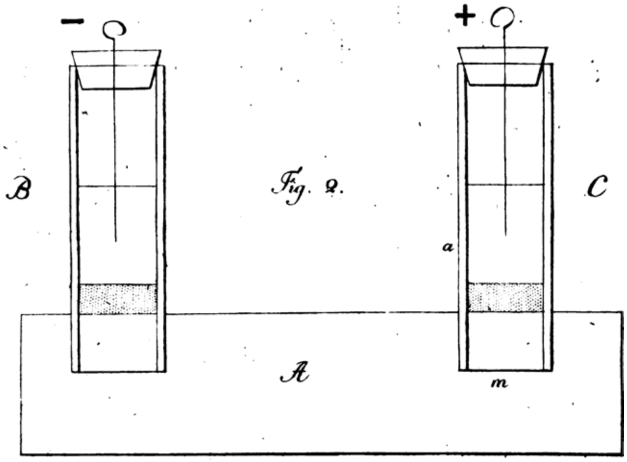

Figure 5. *B* and *C* are two water-filled tubes (of circ. 3 cm i. d., placed at a distance of about 14 cm), plunged in a clay base, *A*, the arrangement used by Reuss in his second experiment on electroosmosis. The stippled portions in *B* and *C* are sand layers. The wires of the + and the – poles are immersed into the water. Reproduced from Reuss, ref. [48]. For details, see text.

Even mor importantly, he also observed a slow rise of the water level at the side of the tube with the negative pole *b*, and an according decrease of the level at the positive pole *a*. Disconnection of the wires led to a reversal of the flow due to gravity, reconnection reproduced the initial effect of the rise of the water level. After fourteen hours, the tube at positive pole *a* was empty, while that at pole *b* was completely filled with water. After four days the experiment was concluded, the wires were disconnected and the initial state with the equal water levels was reconstituted within a few minutes. The results of this experiment unequivocally confirmed the occurrence of electroosmosis (here with a flow of the liquid towards the negative pole[31]), a phenomenon Reuss termed *motus stoechiagogus*.

In his second experiment Reuss filled a block of moist clay into a container (*A* in Figure 5) and inserted two glass tubes. The bottoms of the tubes were covered by thin layers of carefully washed sand (indicated by shaded zones in the Figure), and the tubes were filled by 3 cm with water. Platinum wires were inserted into the centers of the tubes through their open ends (plugged with corks), and were connected to a Voltaic pile.

After completion of the current, the clay first began swelling and softened to mud at the bottom of the tube with the positive pole; in the following the penetration of the sand layer by clay particles was observed under formation of a pointed mound at position *a* in the Figure. Muddy liquid was separating from the mound and formed a mud layer at the surface of the sand. This process occurred only in the tube with the positive pole, but no effect was noticed in the other tube. Upon continuation of the experiment for four days, electroosmosis of water from the positive to the negative pole was observed, most probably caused by the same source as in the first experiment, *viz.* by the negatively charged quartz sand (see footnote 31).

The question now arises whether electrophoresis or electroosmosis was causing the transport of the clay particles through the sand layer into the tube with the positive pole. Reuss attributed the penetration of the clay to electroosmosis. Since commonly the clay particles (like quartz

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[31] In this experiment of Reuss, the electroosmotic flow of the liquid towards the negative pole has its cause in the negatively charged surface of the quartz sand which he inserted into the tube. The sand consists of silica, polymerized silicic acid, which possesses residual silanol groups at its surface. This groups have weak acidic property and dissociate in the presence of water into negatively charged silanolate groups ($\equiv$Si-O^{-}). These groups are the sources of the fixed negative charges at the surface of the quartz sand, which is the one side of the so-called electrochemical double layer. In electroosmosis positive ions dissolved in the liquid phase compensate the negative charges, but due to their thermal energy they are not rigidly attached at the solid surface, and always at least a fraction of the cations is freely movable. If a tangential electric field is applied, the free cations are attracted towards the cathode due to electric forces dragging a layer of water into the same direction, which represents the first water layer flowing by electroosmosis. Due to viscosity forces, the flow impulse is transferred to each adjacent water layer into the bulk of the liquid, and within shortest time the entire liquid is flowing by electroosmosis. In the present case of quartz, water is driven by the cations of the interfacial double layer towards the negative pole. It is interesting that electroosmosis was originally discovered by crystallized silica as described above, because the same material, in its amorphous form, named fused silica, is the universal choice for the common narrow open tubes used in contemporary capillary electrophoresis. In this separation method, the electroosmotic flow is a fundamental component of the separation set-up utilizing the migration of the analytes.

sand) are negatively charged,[32] electroosmotic flow caused by the porous clay of block *A* in Figure 3, bottom, would be directed towards the negative pole. By reason that the clay particles migrated towards the positive pole electrophoresis, not electroosmosis, was probably the cause of their migration. Thus, the first observation of electrophoresis had to be attributed to Reuss, and not to Porrett.

But by midst 19th century only few scientists drew attention to Reuss´ work, amongst others Gustav Heinrich Wiedemann and Georg Hermann Quincke, reputed scientists in the field. In a paper from 1861 entitled "*Ueber die Fortführung materieller Theilchen durch strömende Electricität" ("On the transport of material particles by flowing electricity"*. Quincke asserted that[10]

> … Reuss in Moskau beobachtete zuerst, im Jahre 1807 daß ein galvanischer Strom Flüssigkeiten in der Richtung des positiven Stromes mit sich fortführte, wenn die Flüssigkeit an einer Stelle durch eine poröse Scheidewand unterbrochen war. Seine Beobachtungen scheinen jedoch bis in die neuste Zeit hinein wenig bekannt geworden zu seyn, so daß oft Porret, der 1816 ganz ähnliche Versuche beschrieben hat, als der Entdecker dieser später auch wohl mit dem Namen „elektrische Endosmose" bezeichneten Erscheinungen angesehen wird…[33]

In this comment Quincke referred to an unpublished lecture entitled "*Indicium de novo hucusque nondum cognito effectu electricitatis galvanicae" ("Notice of a new, hitherto unknown effect of galvanic electricity")* which Reuss held in November 1807 before the Physical-Medical Society, Instituted at the Moscow Imperial University of Letters.[51] It should nevertheless be pointed out, that although the first observation of electroosmosis should be attributed to the 1807 work of Reuss,[34] Porrett wrote his 1816 paper without any knowledge of its existence.

Interestingly, the history about the discovery of electroosmosis and electrophoresis does not end here. The complete story has been reported recently in a carefully researched and informative essay by Christian Biscombe.[52] The author referred to yet another nearly disregarded report by Nicolas Gautherot, which found only a passing mention by Humphry Davy in his Bakerian Lecture,[35] read November 20, 1806 (ref. [53], p. 20). Gautherot was born in 1753 in Is-sur-Tille (Côte-d'Or)**,** France, in a poor family. He became a well-known composer and musician by profession (in 1799 he published a book entitled "*Théorie des sons*"[54]), and an amateur chemist by interest. Fascinated by the newly discovered galvanic electricity (he was member of the *Société galvanique*, founded in 1802), he had carried out some experiments around 1800. One of his very few reports was read by him at March 17, 1801 (*26 ventôse an 9*) at the *classe des sciences de l'Institut des Sciences, Lettres et Arts*, entitled "*Mémoire sur le Galvanisme*"[55] and published in 1801, only one year after Volta´s publication of his pile. We find the relevant part of Gautherot´s experiments on pages 205 and 206 of ref. [55], which reads

> … Voyant que les plaques métalliques sont fortement oxidées lorsque la pile ou la batterie galvanique a été pendant quelque tems soumise aux expériences, j'ai voulu voir d'une manière plus particulière l'influence de l'attouchement des métaux pour la décomposition de l'eau. Pour cet effet, j'ai placé sur les deux côtés opposés d'une plaque carrée de zinc deux petites bandes de carton pour supporter une plaque d'argent de même dimension que celle de zinc. J'ai place une goutte d'eau entre ces plaques, de sorte qu'elle touchait aux deux métaux. En examinant de tems en tems ces plaques, je ne me suis point apperçu, même au bout de soixante-douze heures, d'aucun effet d'oxidation; tandis qu'un autre appareil disposé de même, avec cette seule différence qu'il y avait une légère communication métallique entre les deux plaques, l'oxidation commencait déjà à être sensible au bout seulement de huit minutes. Ici, l'oxide de zinc, quoi que d'une pesanteur spécifique supérieure à celle de l'eau, abandonne le zinc qui est à la partie inférieure, pour adhérer à l'argent en y dessinant le contenu de la goutte d'eau. Si l'on a laissé écouler assez de tems pour que l'oxide de zinc soit plus abondant, une partie seulement adhère à l'argent, et le reste parait former dans l'eau des espèces de grumeaux gélatineux."[36]

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[32] In his textbook from 1909, W. Ostwald summarized the charge of colloidal particles as follows: " … *So erweisen sich bei reinem Wasser als Dispersionsmittel … als negativ: …die meisten dispersen festen Stoffe wie ..., Stärke, Quarz, Feldspat, Ton, Kaolin,…*"; ref. [50] W. Ostwald, *Grundriss der Kolloidchemie*, Theodor Steinkopff, Dresden, **1909**., p. 233 ("*Thus, with pure water as the dispersant … are negative: … most of the disperse solids, such as … starch, quartz, feldspar, clay, kaolin, …").*

[33] *"… Reuss in Moscow observed, in 1807, as first that a galvanic current transports liquids in the direction of the positive current, given that the liquid is divided at one position by a porous membrane. His observations, however, seem to have become little known until very recently, so that often Porret, who in 1816 described very similar experiments, is regarded as the discoverer of these phenomena, later also termed electric endosmosis."*

[34] A fact deserves to be mentioned which is nearly always ignored in the context of Reuss` investigations about electrokinetic phenomena. It is his collaboration with the Russian scientist Pjotr Ivanovich Strakhov [1757-1813], who held the chair at the newly-created Institute for Experimental Physics at the Moscow University since 1791. Strakhov was well-known – in addition to his research in other fields – for his observations of electrical conductivity of water and earth.

[35] In a single sentence Davy mentioned that "*M. Gautherot has stated, that in a single Galvanic circle of zinc, silver, and water, in an active state, the oxide of zinc formed is attracted by the silver;*"

[36] *"… Seeing that the metal plates are strongly oxidized when the battery or the galvanic battery has been subjected to experiments for some time, I wanted to see in a more particular way the influence of the touching of the metals on the decomposition of the water. For this purpose, I placed two small strips of cardboard on two opposite sides of a square plate of zinc to support a silver plate of the same size as that of zinc. I placed a drop of water between these plates, so that it touched the two metals. In examining these plates at times, I did not perceive, even at the end of seven-*

We interpret and comment this experiment as follows.[37] At first, Gautherot horizontally arranged a zinc and a silver plate of equal size, the former below the latter, both separated by a small dry strip of cardboard as non-conducting spacer. Note that, in contrast to a Voltaic element, the cardboard was neither wetted nor impregnated. Gautherot placed a drop of water between the plates such that the drop touched both metals. Note also that the two plates were not electrically interconnected at this stage of the experiment (notwithstanding that the impure water Gautherot had available was certainly conductive). Gautherot registered that even after seventy-two hours no indications of an oxidation could be seen. This is what one expects because no electric circuit was closed.

In contrast to his first one, in a second experiment Gautherot interconnected the two plates with a metallic conductor. Hence, upon closing the circuit by the metallic connection, Gautherot observed oxidation at the bottom zinc plate within eight minutes and assumed that zinc oxide had been formed.[38] That was the so far expected result of electrolysis.

However, at the same time Gautherot observed the detachment of particles of this newly formed material from the zinc surface and – despite their higher specific weight compared to water – their movement upwards through the water drop and their adherence at the upper silver plate. Later on, only a part of the particles stuck at the silver surface, the rest remained in the water, dispersed as "*gelatinous*" clots. This material was probably the well-known typical voluminous and jellylike precipitate of zinc hydroxide.

We might assume from this experiment that the positively charged zinc hydroxide particles[39] which were formed by anodic oxidation indeed migrated in the electric field towards the cathode. If we accept this as a fact (even though the description of the experimental conditions is somewhat vague), Gautherot indeed was first who observed electrophoresis, prior to von Reuß and Porrett.

About two years later, on November 29, 1803 Nicolas Gautherot died, as reported by Urbain René Thomas Le Bouvier DesMortiers,[57] caused by a shock from an electric battery (see ref. [58]).

SUMMARY

Here we present the first of a series of papers on the history of observations and method development in the field of (capillary) electrophoresis. In this contribution we take a journey at the outset of what we coin as the "*1st epoch of electrophoresis*", which we outline as a period of 125 years between the 1780s and the 1910s. Due to the striking coincidence with the same period of European political history we deliberately choose to borrow the term "*Long 19th Century*" from the British historian Eric Hobsbawm (see footnote 7), who coined it for the time from the French revolution in 1789 till the beginning of the First World war in 1914. It is astounding that in the course of this epoch nearly all fundamental concepts, models, hypotheses, theories and laws concerning the electrically induced motion of charged particles (in electrophoresis) and of the transport of the liquid medium (in electroosmosis) were formulated, derived and became well-known. But it is the singular and even more astonishing characteristic of this epoch that no approach has been undertaken to utilize all this knowledge for the separation of constituents of a mixture.

It has to be recalled that electrophoresis *by itself* is a drift of charged particles – dispersed in a liquid – under the influence of an electric potential difference. The only specific of *capillary* electrophoresis is that the motion takes place within an open narrow tube, but it is still obeying the general laws of electrophoresis. It is further to note that capillary electrophoresis as we know it from the midst of the 20th century, was first performed as early as in the 1860s, albeit not for separation purposes. As the basic principles of electrophoresis, though it was not named as such, came into the focus of research at about 1800, we find it appropriate to include here the history of the general physical and chemical principles on which it is based.

In the years from 1800 to 1816 three electrically-

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ty-two hours, any effect of oxidation; while at another apparatus arranged likewise, with the only difference that there was a slight metallic contact between the two plates, the oxidation already began to be sensible after only eight minutes. Here, the oxide of zinc, although of a specific gravity greater than that of water, abandons the zinc from the bottom part, and adheres to the silver by drawing the content of the drop of water. If enough time has elapsed for the oxide of zinc to be more abundant, only a part adheres to silver, and the rest appears to form gelatinous lumps in water."

[37] Please note that the authors use a terminology in the present interpretation and comments which was not known at Gautherot´s time.

[38] It was probably sparingly soluble zinc hydroxide formed by the zinc ions due to anodic oxidation which were released into the solution. The solubility product of $Zn(OH)_2$ is 3.10^{-17} $mol^3.L^{-3}$. The measured concentration of dissolved free Zn^{2+} ions in water at pH between 6 and 7 and ambient temperature is a few hundred $\mu g.mL^{-1}$ (it is lower than that calculated from the solubility product), see ref. [56] G. Dietrich, *Hartinger Handbuch Abwasser- und Recyclingtechnik*, 3rd ed., Karl Hanser Verlag, München, Wien, **2017**..

[39] This is in accordance with the summary of Wolfgang Ostwald in his standard text book about one century later, which we have cited in the context of clay in Reuss´ experiments: "*So erweisen sich bei reinem Wasser als Dispersionsmittel… als positiv: alle Metallhydroxyde*" (ref. [50] W. Ostwald, *Grundriss der Kolloidchemie*, **1909**., p. 233 ("*Thus, with pure water as the dispersant … all metal hydroxides turn out to be positive*").

induced phenomena were observed upon the application of an electric potential difference to a liquid containing charged or chargeable particles: electrolysis at the electrodes, electrophoresis in the liquid dispersion of the charged particles, and its converse phenomenon, electroosmosis (an electrically-induced transport of the liquid relative to charged surfaces). All these discoveries relied on a source of a constant-flow electricity, not on the static electricity known at the time. This new source was provided by the Voltaic pile, which transformed chemical into electrical energy upon a contact between two different metals with a moistened layer of spongy material in between. It was invented by Alessandro Volta, prompted by Galvani´s incorrect theory of an *animal electricity* published in 1791. We find it thus justified that with this context the history of electrophoresis, and that of capillary electrophoresis commenced.

The discovery of electrolysis is attributed to William Nicholson and Anthony Carlisle, who in 1800, while trying to copy Volta´s pile, observed formation of gas bubbles as a result of the decomposition of river water by galvanic electricity. The history of the discoveries of electrophoresis and electroosmosis is far more intricate. Chronologically, electrophoresis was first observed in 1801 by an amateur chemist, Nicolas Gautherot, who observed motion of small particles (probably zinc oxide or hydroxide) formed at a zinc plate towards a silver plate upon connecting the two by a metal conductor. To his misfortune, however, his experiments were almost completely ignored by the scientific community, he was never cited as discoverer of electrophoresis (mentioned only briefly by Davy´s Bakerian lecture in 1806) and died as a result of electric shock from a battery.

In 1807 Ferdinand Frédéric Reuss (Ferdinand Friedrich von Reuß) reported unexpected generation of flow of water within a V-shaped tube covering its bottom part with quartz sand. After closing the circuit, the water level at the one side of the tube raised, whereas that at the other side decreased accordingly. Upon inverting the polarity, the reversed effect of the water levels occurred. Thus, Reuss unequivocally discovered the phenomenon of electroosmosis. In a second experiment, he placed a quartz sand layer above wetted clay in two water-filled tubes, each with wires dipped into the water as poles. Upon connecting the poles to a Voltaic pile he observed movement of clay particles through the sand. During these experiments Reuss inadvertently, yet undoubtedly, observed both electroosmosis and electrophoresis.

Chronologically, Robert Porrett was the tritagonist in the cast of the play about the priority of the discovery of these electrically-induced phenomena. In 1816 Porrett, not aware of any of the previous discoveries, observed a transport of water from one chamber of a divided jar to another chamber through a bladder divider upon connecting the chambers to the poles of a Voltaic pile. Upon publishing his observation in *Annals of Philosophy*, he gained attraction in the scientific community and up until the middle of the 19th century has been regarded as the discoverer of electroosmosis, in contradiction to the historical facts. It is to note that just as Reuss had no knowledge of Gautherot`s prior experiment observing electrophoresis, neither Porrett was aware of Reuss' priority in discovering electroosmosis.

The above experiments revealing the phenomena of electrolysis, electrophoresis and electroosmosis were merely observatory and offered no formulations of hypotheses on their underlying causes. It is thus expectable that the scientific interest that followed in the subsequent years and decades was directed towards their principles and origins. After the discovery of electrolysis the research on the motion of ions[40] was immediately intensified. Attempts at theories about their inseparable connection, which may have led to an understanding of ion migration, and were undertaken between 1800 and the 1830s, will therefore be the subject of Part 2 of the first series of our historical reviews.

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[40] *Ion* is also a term which was not known at that time. Humphry Davy, one of the leading physicist and chemist at his time, described the nature of ions in a Bakerian lecture in 1807 as follows: *The body possessing the positive energy being repelled by positively electrified surfaces, and attracted by negatively electrical surfaces; and the body possessing the negative energy following the contrary order. (ref. [53] H. Davy, Phil. Trans. Roy. Soc. (London)* ***1807****, 97, 1-56., p.33)*

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