The Silver Voltameter:

An Essential Instrument for the Definition of the Unit of Electric Current

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Abstract

We discuss the restoration of a silver voltameter belonging to the Historical Collection of Physics Instruments of the University of Palermo. We stress the essential role this instrument had in the definition of the unit of electric current.

Introduction

The discovery of the 'electric fluid', by Stephen Gray (1666 – 1736) in 1729, and the invention of the pile, by Alessandro Volta (1745 – 1827) in 1800, opened the way to the investigation of a new class of phenomena connecting electricity with chemical reactivity. In the same year, Anthony Carlisle (1768 – 1840) and William Nicholson (1755 – 1815) carried out the first electrolysis, giving rise to a comprehensive investigation about the possibility of using electricity to realize chemical transformations.

Three decades later, Michael Faraday (1791 – 1867) stated a direct proportionality between the amount of electricity and the amount of substance it could chemically decompose:[1] this proportionality is summarized in the well-known Faraday's electrolysis laws. Soon after, he built an apparatus to determine the amount of electricity flowing through it. According to Faraday, water is the most suitable substance to determine the amount of electric charge, since it is easily decomposed, especially if some salt or acid is dissolved in it to improve its electrical conductivity[1]; furthermore, its decomposition products do not suffer any interference and, as they are in the gaseous state, they can be easily collected and weighted.

The instrument consisted, essentially, of a V-shaped glass tube, containing a dilute sulphuric acid solution, into which two platinum sheets, or two platinum wires, were immersed, nearly touching each other, and connected in series with the electric circuit. Faraday called the instrument 'Volta electrometer', a name which was afterwards abbreviated to voltameter by John Frederic Daniell (1790 – 1845).[2]

The Silver Voltameter

In 1835, Carlo Matteucci (1811 – 1868) realized the first silver voltameter, which he used to measure the electric current flowing through a circuit. The instrument consisted of two platinum sheets, dipped, at the same extent, in a silver nitrate solution; to determine the amount of electricity which was delivered during an electrolysis, at the end of the process, the weight of the metallic silver, deposited at the negative electrode, was determined.[3]

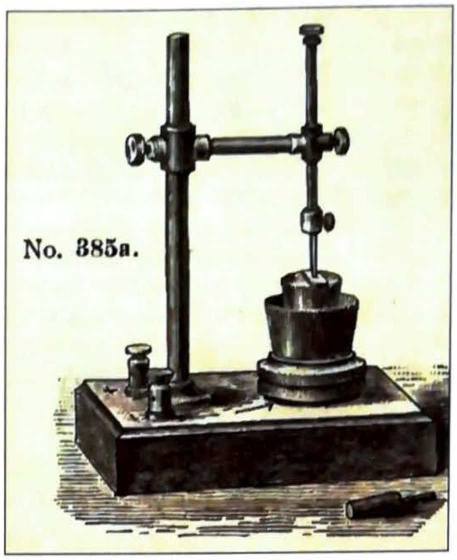

Fig. 1 *A drawing of a Poggendorff type silver voltameter, as shown in the 1894 Hartmann & Braun Catalogue of Electrical Measuring and Test Instruments.*[5]

The most popular type of silver voltameter was realized by Johann Christian Poggendorff (1796 – 1877) and described, for the first time, by Gustav Heinrich Weidemann (1826 – 1899) in his treatise on galvanism published in 1872.[4] The apparatus was composed by an adjustable stand, on a wooden base, provided with electrical terminals; the stand held a vertical rod, over a small platinum bowl. At the end of the rod, there was a silver rod (or silver strips), which could be lowered into the platinum bowl. The cathode - the platinum bowl - was located on a metallic support on the wooden base, directly connected to the negative pole; it was filled with an aqueous 10-20% silver nitrate solution, into which the anode – the silver rod – was dipped. Fig. 1 shows a drawing of a Poggendorff type silver voltameter, from the 1894 Hartmann & Braun Catalogue of Electrical Measuring and Test Instruments.[5]

The dry platinum bowl was initially weighted and filled with the solution; then electric current was passed for a measured time. The flowing electric current oxidized the metallic silver anode to silver nitrate and deposited metallic silver on the cathode bowl. As silver ions were generated by the anode dissolution, and deposited on the platinum bowl, their concentration in solution kept constant.

At the end of the electrolysis process, the platinum bowl was emptied, cleaned in an alcohol-water mixture, and dried in a hot-air bath at about 160°C; then it was placed on a triangle, resting on the rim of a vessel

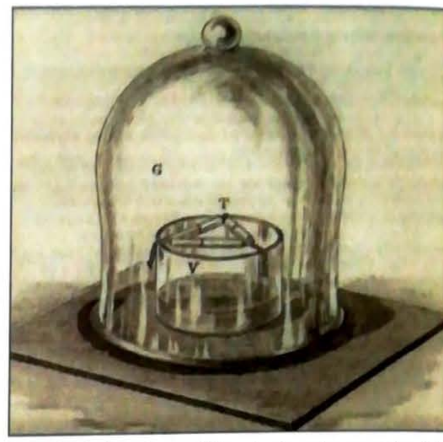

Fig. 2 *A drawing of the desiccator used with the silver voltameter.*[7]

which contained strong sulphuric acid, calcium chloride, or other water-absorbing substances; finally, the whole was covered with a bell jar. After cooling in the desiccator, the platinum bowl was weighted again to obtain the deposited amount of silver as increase in its weight.[6,7] Fig. 2 shows the desiccator used with the silver voltameter.[7]

To convert the weight of the deposited silver into amount of current, an accurate knowledge of the silver electrochemical equivalent was needed. Electrochemical equivalents had been defined, in 1833, by Faraday, as the weight ratio of two different substances deposited by the same current: '*I have proposed to call these bodies generally ions, ... and the numbers representing the proportions in which they are evolved electrochemical equivalents*'[8]; in 1840, Wilhelm Eduard Weber (1804 – 1891) used the term electrochemical equivalent to denote the amount of electrochemical action produced by one unit of current in unit time.[9]

The silver electrochemical equivalent was determined, for the first time, by Friedrich Kohlrausch (1840 – 1910) in 1873 and, then, in 1884, by Lord Rayleigh (1842 – 1919), together with Eleanor Balfour Sidgwick (1845 – 1936), using an improved Poggendorff silver voltameter. The anode was wrapped up with a sheet of filter paper, to avoid that metallic silver fragments could break down from the anode and fall into the platinum bowl, thus introducing a positive error in its weight determination.[10]

In his accurate work of reviewing atomic-weights values, Theodore William Richards (1868 – 1928) furtherly improved the apparatus, to prevent impurities diffusion toward the cathode, by introducing a porous cylinder around the silver rod. Using this cell, put in series with other types of voltameters, Richards determined the silver electrochemical equivalent as 1.1175 milligram per coulomb, and the value of the Faraday constant as 96580 coulomb per gram equivalent, suggesting changing the old term of voltameter into coulometer.[11,12]

The silver voltameter has been used for long time to calibrate ammeters by measuring the amount of silver which is deposited in an electrolytic cell in a known time. To calibrate the ammeter, the voltameter is connected in series with the instrument to be calibrated, so that the current, in both devices, is the same.

Accurate investigations in England, France, Germany and United States greatly improved the precision of the silver voltameter, which was used to define an important fundamental physical quantity: the unit of electric current, denominated ***ampere*** by the First International Conference of Electricians (Paris, 1881).[13] In 1893, the International Electrical Congress, in Chicago, assessed the unit of electric current, called ***international ampere***, as the unvarying current which, when passed through a solution of silver nitrate in water, deposits silver at the rate of 0.001118 of a gram per second.[6] In 1908, the international ampere was better defined, as the current that deposits 0.001118000 grams of metallic silver per second from a solution of silver nitrate in water.[12] The ampere was adopted in 1948 by the International Weights and Measures Committee as one of the seven fundamental units of the International System; it was defined as the constant current that, flowing in two identical parallel conductors of infinite length, of negligible section, disposed at one meter each other in vacuum, would produce a force of 2×10^{-7} newton per meter.[13]

The Voltameter of the Historical Collection of the University of Palermo

The Historical Collection of Physics Instruments of the University of Palermo, displayed at the Department of Physics and Chemistry, collects about 500 instruments and apparatus.[14] Beside its historical value, the collection gives students the opportunity to have hands-on learning experiences and insight into career options.[15] Although the collection has been mostly catalogued, several instruments still need to be restored and included into the catalogue. An uncatalogued Poggendorff type silver voltameter and the accompanying desiccator have recently been restored. The silver voltameter, signed by Hartmann & Braun[16], is composed by an adjustable stand, on a rectangular mahogany base (12 × 20 × 20 cm) with electrical terminals, which holds a vertical brass rod over a small platinum bowl. At the end of the brass rod, there is the silver rod that

Fig. 3 *The Hartmann & Braun logo engraved on the front side of the wooden base.*

can be lowered into the platinum bowl. The Hartmann & Braun's logo, shown in Fig. 3, is engraved on the frontal side of the wooden base. On the back side, the company's name, Hartmann & Braun, is engraved. This kind of silver voltameter was used to measure currents up to 0.25 A; for larger currents, copper voltameters, having electrode surface of about 200 cm^2, were preferred.

The desiccator consists of a bell jar, 10 cm in diameter and 10 cm in height, on a circular wooden base, 17 cm in diameter and 5 cm in height, into which a circular hole houses a ceramic basin containing the drying substance. The basin is fixed to the base by a brass triangle, which holds the platinum bowl. The bell jar and the wooden base are tightly connected,

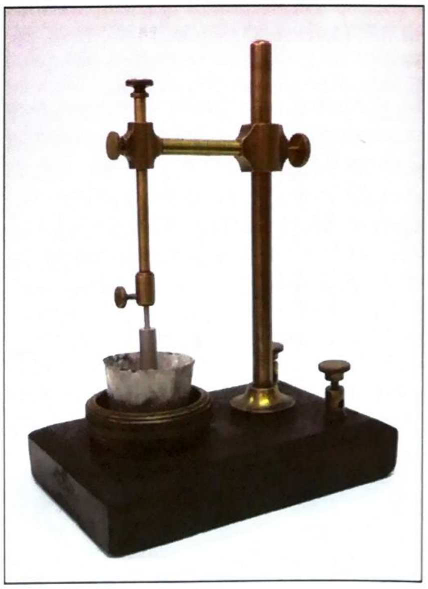

Fig. 4 *The silver voltameter, after the restoration and assembling work.*

to prevent environment humidity enter the bell.

On the voltameter, there is no label indicating an inventory number or a purchase date. However, in the archival documents of the former Istituto di Fisica, we found the record (BUONO DI CARICO N. 180, 7.9.1893, Lire 90) of the purchase of a non-specified Voltameter (INV. No. 477) by the Director Damiano Macaluso (1845 – 1932). Since a similar item was produced in the same period by Hartmann & Braun and advertised in their 1894 Catalogue, we may infer that the silver voltameter, very probably, is that reported in the archival documents of the Istituto di Fisica.

On the desiccator are glued two inventory labels, whose numbers are completely deleted. Furthermore, the instrument is not signed. However, it is reasonable to infer that both instruments were used together and, hence, are from the same period. Probably the instruments were used to calibrate ammeters, but, so far, we have not found, in the scientific literature, papers describing the use of these instruments at the University of Palermo.

The restoration work has mainly concerned the cleaning of all parts, and has been carried out by applying different procedures, depending on the materials. The following interventions have been done.

- Removal of surface deposits with the use of soft brushes.
- Surface cleaning of the wooden parts with an aqueous solution of non-ionic surfactant, at a concentration of about 2%.
- Cleaning of lacquered-brass elements with white spirit (refined kerosene) and cotton cloth.
- Cleaning of the glass bell jar and the ceramic basin with alcohol.

Fig. 5 *The desiccator, after the restoration and assembling work.*

• Upon completion of cleaning process, since the lacquer of the wooden base of the silver voltameter was very damaged, it was protected with a specific wax for wood restoration.

To recover the original aspect of the silver voltameter, to facilitate the understanding of the operating principle by the less-experienced audience, and to contribute to the cultural valorisation of the instrument[17,18], we have built the missing parts; in particular, we have built a silver-plated brass rod, to replace the original one, and used a coeval platinum bowl of similar dimensions as the original one. The instruments, after the restoration process, are shown in Figs 4 and 5, respectively. Once completed the restoration work, the instruments have been placed in the exhibition halls of the Department of Physics and Chemistry.

In conclusion, we have presented the restoration process of a silver voltameter, built by Hartmann & Braun at the end of the 19th century, and a coeval desiccator of an unknown firm. Furthermore, we have discussed the valuable importance of the silver voltameter for the definition of the unit of electric current, the international ampere.

Acknowledgements

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16. Hartmann & Braun Company was founded in Germany in 1879, becoming a leading supplier of scientific instruments by the turn of the century. In the 1920s, Hartmann & Braun expanded its offering to control equipment and, since then, is a leading supplier of both instrumentation and control equipment to the German and pan-European markets.

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Current and Future Events

Details of future events, meetings, exhibitions, etc. should be sent to the Editor. For up-to date information of Society's events, see the SIS website, www.sis.org.uk.

Wednesday 7 February 2018, Cambridge, UK

Afternoon visit to the Whipple Museum of the History of Science. Curator Joshua Nall will give a tour of the special exhibition *Astronomy & Empire*, and there will be a 'hands-on' session featuring recent acquisitions by the museum and a 'mystery object' for members to help identify. Details will be on our website in early January and will also be circulated by email.

Sunday 13 – Friday 18 May, Athens, Greece.

The Society's International Study Tour for 2018 will take place in Athens, Greece. A full itinerary and booking form is available in this issue. Cost: £450 per person (£475 for non-members) to include all excursions, coach travel, lunches and the gala dinner. Delegates will need to arrange their own travel and accommodation. Please complete the enclosed booking form and return with your payment by **23 March 2018** to the Executive Officer. Please do save the date for your diaries.

Thursday 17 May 2018, Teddington, UK

The NPL (National Physical Laboratory) is opening its doors to the public. This is a good opportunity to explore the laboratory and see first-hand some of the amazing research that is carried out. You will need to register before going and they can do this in early 2018. The NPL is ten minutes' walk from Teddington station. For details see http://www.npl.co.uk/openhouse/ But be warned, this Open Day does clash with the Society's Study Trip to Athens.

One of Margaret Watts-Hughes' 'Eidophone' (a voice print) held up for inspection by Chris Parry at Cyfarthfa Museum at Merthyr Tydfil. *See p. 38.* *Photo Robert Wismer.*