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REVIEW ARTICLE

MARTIN MARTENS

Botany, galvanism, and inorganic chemistry

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Botánica, galvanismo y química inorgánica.

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ABSTRACT

Martin Martens (1797-1863) was a Belgian chemist and botanist who studied the oxychlorides obtained by the action of chlorides on metal oxides, and the theory regarding their formation. Chlorine decomposed calcium chloride at a temperature below 200 ºC and calcium hydroxide at a lower temperature. In the presence of water the bleaching compounds generated by the combination of chlorine and alkaline oxides, behaved under all circumstances as the less stable combinations of chlorine with the alkaline bases. Oxychlorides acted upon vegetable and animal substances more or less in the same manner as free chlorine. Oxychlorides were very unstable and could exist only in solution. Martens also studied the phenomena associated with galvanism and electrolytic cells. He proved that simple contact between two heterogeneous bodies, without chemical reaction, was able to develop electricity. He also confirmed the fact that the electromotive force of metals acted in the same direction as the electromotive force of acid liquid conductors. He studied the phenomena observed when boiling an aqueous solution of HCl and the phenomenon of azeotropism, well before it was definitely interpreted. According to Martens, all coloring phenomena taking place in leaves could be explained by admitting that chlorophyll contained two coloring substances, one blue and the other yellow, which could form separately in different cells. These coloring substances were probably transported to the surface of the plant by aqueous transpiration. Martens also developed a two-stage analytical procedure for the chemical-legal analysis of wheat flour.

Keywords: bleaching; chlorophyll; leaves coloration; galvanism, oxichlorides; wheat fluor.

RESUMEN

Martin Martens (1797-1863) fue un botánico y químico belga que estudió la acción de los cloruros sobre los óxidos metálicos y la teoría de su formación. El cloro descomponía el cloruro de calcio bajo los 200 ºC y el hidróxido de calcio a más baja temperatura. En presencia de agua los compuestos blanqueadores generados por la combinación de cloro con los óxidos alcalinos, eran siempre las combinaciones menos estables del cloro con esas bases. Los oxicloruros actuaban sobre las substancias vegetales y animales más o menos en la misma forma que el cloro libre. Los oxicloruros eran muy inestables y solo podían existir en solución. Martens también estudió los fenómenos asociados con el galvanismo y las celdas electrolíticas. Demostró que el simple contacto entre dos cuerpos heterogéneos, sin reacción química, era capaz de generar electricidad. También confirmó que la fuerza electromotriz de los metales actuaba en la misma dirección que la fuerza electromotriz de los conductores líquidos acidificados. Estudió el fenómeno asociado con la ebullición de una solución acuosa de HCl y el fenómeno del azeotropismo mucho antes de que fuera interpretado en forma definitiva. De acuerdo a

Martens, todos los fenómenos asociados con la coloración de las hojas podían ser explicado suponiendo que la clorofila contenía dos colorantes, uno amarillo y el otro azul, que podían formarse en celdas diferentes. Estas substancias colorantes eran probablemente transportadas a la superficie de la planta por transpiración acuosa. Martens también desarrolló un proceso analítico en dos etapas para el análisis químico-legal de la harina de trigo.

Palabras clave: blanqueo; clorofila; coloración de hojas; galvanismo; harina de trigo; oxicloruros

INTRODUCTION

Life and career (Pire, 1863)

A paper by the botanist Louis Pire seems to be the only one containing some information about the life and career or Martin Martens (Pire, 1863). Most of the following material is taken from this source. Martin Martens (Figure 1) was born in Maastricht, Netherland, on December 8, 1797. After taking his basic education in Maastricht, he studied mathematics and physics under Jean Pierre Minkelers (1748-1824) at the Central School of Maastricht, and then entered the Faculty of Medicine of the University of Liege. While preparing for his final examinations he took part in two admission competitions, one at the Faculty of Medicine and the other at the Faculty of Sciences. The two memories he presented for this purpose were crowned and inserted in the *Annales de l'Université*. After receiving his degree in medicine he moved for some time to Paris and then returned to Maastricht where he practiced medicine from 1823 to 1835. In 1824 the Académie des Sciences et Belles-lettres of Bruxelles awarded him a silver medal for a publication about mathematics. In the same year he was elected member and secretary of the Medical Commission of Limbourg and member of the administration council of the Athénée Royale of Maastricht.

Afterwards, he was appointed professor of pharmacology and pharmaceutical chemistry at the provincial school of pharmacy of Maastricht, and member of the Statistics Commission of the Netherlands. In 1834 the Académie Royale of Belgium awarded him a gold medal for his memoir about the chlorides of soluble oxides (Martens, 1836) and shortly thereafter elected him member of its sciences section. In 1835 he moved to Louvain to become professor of chemistry and botany at the Catholic University of Louvain. In 1841 he was appointed member of the newly created Belgian Académie de Medicine. In 1844 the King of Belgium appointed Martens chevalier of his order (Ordre de Léopold). In 1848 he was appointed director of Botanical Garden of Louvain. Two of his most important papers as a botanist (regarding ferns and other plants of Mexico), were published in collaboration with Henri Guillaume Galeotti (1814-185) (Martens & Galeotti, 1842, 1842-1851). Martens passed away on February 1865.

Scientific contribution

Martens wrote about 80 papers, booklets, and books about his research activities in the areas of inorganic chemistry, electrochemistry, botany, animal physiology, agriculture, etc. In addition to the subjects described below Martens also discussed the relation between affinity and molecular composition of compounds (Martens, 1835a); proposed a new scheme for the classification of chemicals (Martens, 1837b); the influence of cohesion and masses on chemical reactions (Martens, 1839ab); the role of the electrochemical theory and its relation to the law of substitutions (Martens, 1850b), the origin and nature of heat (Martens, 1854), the nature of simple bodies (Martens 1861), etc.

Chlorine compounds with oxygen and sulfur

In 1835 Martens read to the Académie des Sciences of Bruxelles a long memoir (74 pages) about oxychlorides, detailing the results of his experiments about the action of chlorine upon metallic oxides, the effect of heat, air, oxyacids, and hydrogenated substances (e.g. hydrogen sulfide and ammonia) upon oxychlorides, the action of oxychlorides upon metallic salts, and a discussion of the prevailing theories about the composition of oxychlorides, (Martens, 1835b).

In this memoir, Martens reported a variety of interesting and unknown facts. For example, although it was long known that at high temperatures chlorine reduced all the basic metallic oxides, generating the pertinent chloride and oxygen, no one had reported the precise temperatures at which these reactions took place. Martens determined this temperature by passing a stream of dry chlorine over oxides such as quicklime barite, and also determined the nature of the products of the reaction. He also found that at room temperature chlorine did not react with the anhydrous metallic oxides, but in contact with their hydroxides a live reaction took place, with formation of the bleaching compounds known as oxychlorides. Some of these reactions occurred only when the hydroxide was dissolved in water. Passing a stream of chlorine over fragments of dry KOH resulted in the formation of a mixture of potassium chloride and potassium chlorate, a non-bleaching mixture. Most of the oxychlorides were soluble in water and their solutions could be obtained by bubbling chlorine through a solution of the soluble oxide. In this situation, a remarkable event took place: the solutions of oxychlorides could not be obtained highly concentrated because the resulting oxychloride decomposed spontaneously into a chloride and a chlorate. This phenomenon would occur whenever one or both of the resulting salts were insoluble in water. This particular result could be used as an alternative procedure for preparing potassium chlorate, a very valuable compound, and also to prove that Liebig was wrong in assuming that the production of potassium chlorate by double decomposition with the help of calcium oxychloride did not require, as claimed by Liebig, the previous thermal decomposition of the oxychlorides into calcium chloride and calcium chlorate (Liebig, 1832). The composition of the gas released when heating calcium oxychloride, varied with the temperature level; up to 100 ^{0}C it contained only pure chlorine; afterwards it was mixture of chlorine and oxygen, finally, at about 150 ^{0}C, near the end of the reaction, the gas released was pure oxygen. The solid residue did not contain calcium oxychloride because it had no bleaching power; it was composed of calcium oxide, calcium chloride, and calcium chlorate (Martens, 1835b).

Air, as such, did not react with oxychlorides; its action was due to the CO_2 it contained. The latter replaced the chlorine little by little and converted the oxychloride to carbonate. The decomposition of potassium and sodium chloride by CO_2, or of the carbonates by chlorine, was completely analogous to the action of a large excess of hydrogen sulfide on an aqueous solution of potassium carbonate: the latter completely displaced the CO_2. Equally, CO_2 completely displaced the sulfide group from potassium or sodium sulfide. Oxychlorides formed combinations, which were very little stable, as shown by the fact they were decomposed by even the weakest acids (e.g. as CO_2) at room temperature, with total elimination of the chlorine. This result suggested that the chlorine was combined with the hydrated metallic oxide. Mixing a solution of calcium oxychloride with another of sulfuric acid resulted in the precipitation of calcium sulfate and release of chlorine (Martens, 1835b).

Martens wrote that the compounds formed by the reaction of chlorine with the hydrated metallic oxides had been long considered to be oxychlorides, and that its composition had to be quite different from a simple union between the chlorine and the oxide. Afterwards, Berzelius had recognized that the compounds formed between sulfur and the alkaline bases were not oxysulfides, but mixtures of metallic sulfides and hyposulfites or sulfates. Hence, considering that chlorine, sulfur, and phosphorus presented very similar chemical properties, Berzelius had postulated that chlorine had to form, with oxides and metallic chlorides, compounds similar to the hyposulfites, that is, *chlorites*, where chlorous acid contained two atoms of chlorine and three of oxygen. According to Martens, this claim had never been confirmed by facts; on the contrary, experience seemed to contradict it; he described a large number of experiments to prove this contention. His results indicated that soluble oxychlorides behaved under all circumstances as compounds of chlorine and a base, that they acted in this manner upon metallic salts, SO_2, H_2S, and ammonia, and that they disinfected and bleached without the presence of an acid able to liberate their chlorine. The fact that chlorites did not have these characteristics left no doubt that they were compounds of chlorine and a metallic oxide and that they did not contain the chlorine as a chlorous acid or oxygen chloride (Martens, 1835b).

Martens summarized his numerous findings as follows: (1) Chlorine decomposed calcium oxide at a temperature below 200 ^{0}C and calcium hydroxide at a lower temperature with release of oxygen. Other alkaline oxides, particularly that of barium, required a temperature near cherry red (about 750 ^{0}C); (2) chlorine was absorbed at room temperature by dry potassium hydroxide as well as by calcium hydroxide, but instead of producing a bleaching oxychloride, like the latter, it generated a mixture of potassium chloride and potassium chlorate; (3) the bleaching compounds generated by the combination at room temperature of chlorine and alkaline oxides, in the presence of water, behaved under all circumstances as the less stable combinations of chlorine with the alkaline bases; (4) most of these compounds existed only in the liquid state or in aqueous solutions, as the oxychlorides of potassium and sodium. Their solutions decomposed spontaneously whenever they could produce an insoluble salt, or when being employed to prepare chlorates; (5) the potassium chlorate obtained by passing a stream of chlorine through a concentrated solution of KOH, was actually the result of the sudden decomposition of the potassium oxychloride previously formed; an spontaneous decomposition totally subordinated to the insolubility of the potassium chlorate in the water that accompanied it. The heat released by the absorption of chlorine in KOH did not influence the formation of the chlorate; (6) potassium chlorate could be advantageously prepared by the double decomposition of calcium hypochlorite and potassium chloride. In this situation potassium chloride and calcium chloride were formed, and by their spontaneous decomposition gave place to the formation of potassium chlorate. This reaction was completely subordinated to the insolubility of potassium chlorate; (7) the production of potassium chlorate by double decomposition with the help of calcium oxychloride did not require, as claimed by Liebig, the previous thermal decomposition of the oxychlorides into calcium chloride and calcium chlorate. The latter reaction, instead of helping, actually impaired the result of the reaction; (8) most oxychlorides were decomposed by heat. The decomposition of solid calcium oxychloride was accompanied by the release of oxygen and chloride; when in the liquid or vey diluted in water, it generated only oxygen. Liquid potassium oxychloride (KClO, potassium hypochlorite) was not decomposed by heat, unless it was so diluted that it could not generate an insoluble salt (potassium chlorate). In every situation, it released only oxygen when heated; (9) oxychlorides decomposed in contact with air by the influence of CO_2, which replaced the chlorine. CO_2 reacted with a solution or KCl or NaCl, yielding first a mixture or a mixed compound of the carbonate and the oxychloride. Its continuing action converted the oxychloride into a simple carbonate: (10) The most weak acids, employed in sufficient amount, decomposed completely the oxychlorides, releasing all the chlorine; (11) sulfur dioxide and hydrogen sulfide acted on oxychlorides in a different manner; their action was the same as that of an aqueous solution or chlorine mixed with an alkali; a further proof that oxychlorides were actually weakly stable compounds of chlorine and a metallic oxide; (12) oxychlorides acted upon aqueous solutions of metallic salts in the same manner as did simple mixtures of aqueous chlorine and alkali; a result that proved the weakness of these two elements; (13) oxychlorides acted upon vegetable and animal substances more or less in the same manner as free chlorine. Their bleaching and disinfectant action could take place without the presence of an acid that decomposed them; and (14) chlorine deutoxide (Berzelius chlorous acid) was able to combine with alkaline oxides the same as chlorine did, but the resulting products were quite different. Some of them could be obtained in crystalline form, which fused over ardent coal as the chlorates, probably as a result of the easiness with which the oxygen chloride released its oxygen; a characteristic not present in oxychlorides (Martens, 1835b). The Académie found Martens' results so important that decided to publish his lecture in its journal *Mémoires Couronnés*.

A short time afterwards, Antoine-Jerôme Balard (1802-1876) published a memoir in which he tried to prove that Martens' conclusions were wrong (Balard, 1834). Balard's discovery of hypochlorous acid and the bleaching properties of the resulting hypochlorites seemed to corroborate that bleaching compounds should be considered as mixtures of hypochlorites and chlorides, and hence, that Berzelius had correctly interpreted their action. This paper led Martens to perform additional experiments and to conclude again that bleaching compounds were actually oxychlorides (Martens, 1836). His main arguments were the following: (a) the chlorine dioxide of certain chemists should be considered an acid under the name chlorous acid. Chlorous acid combined with alkaline oxides to form chlorites; these salts were decomposed by most acids with effervescence and disengagement of chlorous acid; (b) chlorites could be obtained in the solid state by evaporation, without decomposing, as long as they had an excess of base, or, more precisely when they possessed an alkaline action. Saturated (neutral) chlorites, as shown by litmus paper, decomposed into chlorates and chlorides, the same as oxychlorides did, except that they generated more chlorate than the latter; (c) the chlorites were powerful bleaching and oxidizing compounds, the same like the oxychlorides and the hypochlorites of Balard. When unsaturated, they did not destroy color, except when they were in the presence of an acid, The other chlorites bleached instantly, the same as free chlorine; (d) the chlorites, alone, or mixed with metallic chlorides, had all the typical properties that distinguished them from the decolorizing oxychlorides; for example, disengaging chlorous acid instead of chlorine, when in the presence of acid; (e) the reaction of hypochlorous acid with a metallic chloride, also evolved only chlorine; (f) the chlorites had the same bleaching and oxidizing power as Balard's hypochlorites but were much more stable; and (g) The distillation of sodium and potassium chlorides supersaturated with chlorine yielded hypochlorous acid, leaving a residue of a neutral metallic chloride (Martens, 1836).

In 1842 Joseph-Louis Gay-Lussac (1778-1850) published a paper about the bleaching compounds formed by chlorine with the basic metallic oxides, in which he supported

Balard's opinion that these substances were actually a mixture of a metallic chloride and hypochlorite (Gay-Lussac, 1842). Once again Martens had to carry on additional experiences to show that the arguments of Gay-Lussac did not fit the experimental evidence and could be better explained by assuming that the active compound was a hypochlorite (Martens, 1842b).

In a following paper Martens reported that his finding that the hydroxides of potassium, sodium, and calcium were able to react with chlorine to form bleaching compounds composed of one part of base and one of chlorine, but also compounds formed of one part of base and *two* of chlorine, which he had named *oxydichlorides* (Martens, 1843a). These oxydichlorides had double the decolorizing power of the oxychlorides and were easily distinguished from the latter by the easiness of their decomposition into hypochlorous acid and metallic chloride, according to the equation $Cl_4RO = Cl_2O + Cl_2R$, where R represented the metallic radical (at that time chlorine was considered to be monatomic). The neutral oxychlorides of potassium and sodium decomposed under the continuous action of heat into a mixture of metallic chlorate and chloride (Martens, 1843a).

In a final long memoir (63 pages) published in 1844 Martens added the results of his experiments on the preparation of the different bleaching oxychlorides and oxydichlorides, the analysis of their solutions, the action of heat on these chlorides and on hypochlorites, and listed some new consequences of his comprehensive study of the problem (Martens, 1844).[20] According to Martens, (a) alkaline oxides were able to form with chlorine, by the wet way, not only bleaching chlorides composed of one proportion of base and one of chlorine (neutral oxychlorides), but also chlorides more or less defined, having an excess of base or an excess of chlorine; (b) an aqueous solution of the neutral oxychlorides was still able to absorb at 0 ^{0}C additional chlorine to become *oxysuperchlorides* (i.e. the oxydichlorides already mentioned); (c) oxydichlorides were always formed by saturating with chlorine a cold weak solution of the carbonates of sodium or potassium; (d) the oxydichlorides could only exist in solution; they were very unstable; this decomposition was very fast and was accelerated further by heat or by bubbling through the solution a gas different from chlorine; (e) the high instability of oxysuperchlorides prevented their use for medical or industrial purposes; (f) the oxysuperchlorides could be easily distinguished from the neutral or basic oxychlorides, by their fast decomposition; (g) the oxychlorides of potassium or sodium, used as bleaching or disinfectant liquors, should never be prepared by the direct method, but always by the double decomposition with the oxychloride of calcium (basic or neutral), to avoid the presence of an excess of chlorine: (h) the decomposition of a solution of calcium hypochlorite at 100 ^{0}C occurred at a slower rate than the decomposition of the solution of the corresponding neutral calcium chloride; (i) a weak solution of free hypochlorous acid decomposed, at 100 ^{0}C into chlorine and chloric acid, and finally, (j) oxydichlorides should be considered to be a mixture of hypochlorous acid and a metallic chloride, in which all the bleaching ability depended on the hypochlorous acid (Martens, 1844).

Martens also studied the chemical properties of sulfur chlorides (Martens, 1837a). In the opening statements of his paper on the subject he wrote that seven of the known metalloids (oxygen, fluorine, chlorine, bromine, iodine, sulfur and selenium) were considered to be electronegative; they combined with electropositive metalloids to yield acid compounds where the electronegative substance was the acidifying principle. In other words, at the present time there were seven classes of different metalloid acids (i.e. oxacids, fluoacides, chloracids, etc.) and hence it was improper to divide acids into oxacids and hydracids because this classification led to the assumption than in the hydracids the hydrogen played the same role as oxygen in the oxacids. There were other acids, such as the ones listed above, that did not contain hydrogen or oxygen; not only that, compounds such as phosphorus chloride, which were able to react with a strong base such as ammonia to produce a neutral compounds, should also be considered to be acids (in this case, chlorophosphorus acid). Within the same assumption it was appropriate to assume that sulfur chloride was an acid compound because sulfur was more electronegative than phosphorus. All these considerations led Martens to conduct the proper experiments to test this hypothesis (Martens, 1837a).

Although sulfur monochloride and sulfur dichloride reddened strongly litmus paper, this characteristic was not enough to attest their acid character; the clear demonstration was their reaction with ammonia. Martens introduced a stream of dry gaseous ammonia into a dry balloon containing a small amount of pure sulfur dichloride and noted the immediate formation of a thick fume that deposited on the walls of the vessel as a brown flocculent substance, and continued to do so until both reagents had reacted completely. The deposit was found to be neutral, volatile, having a salty prickly taste, and being completely decomposed by concentrated sulfuric acid into sulfur dichloride and ammonium sulfate. This proved that the deposit was a true salt composed of sulfur dichloride and ammonia, which Martens named *ammonium chorosulfate*. The same result was obtained with sulfur monochloride, except that the compound was now ammonium chlorosulfite (Martens, 1837a).

Martens described in detail the physical and chemical properties of both ammonia derivatives. Thus, for example, ammonium chlorosulfate was very soluble in anhydrous alcohol and ether and decomposed immediately when dissolved in water into ammonium hyposulfite and SO_2 (Martens, 1837a).

Galvanic cells

Martens published a large number of papers about electrochemical and electrolytic phenomena (i.e. Martens, 1839c, 1842ac, 1843b; 1845; 1851; 1852b, 1862). Here we describe his first publication on the subject, explaining the manner in which the galvanic cell acted on the decomposition of substances. This publication is important because it depicts the state of the knowledge about electrochemistry prevalent at the time, when Svante Arrhenius (1859-1927) was not born yet.

The memoir was divided in three parts; the first one described the causes capable of generating galvanic currents, the second, the flow and distribution of electricity in piles, and the third, the mode in which a pile decomposed different bodies (Martens, 1839c).

Martens wrote that it was already known that metallic contact was enough to generate galvanic currents, and that this fact had been utilized to conduct chemical decompositions. Some later publications described experiments showing that the contact of metals with liquids able of attacking them chemically, also gave place to galvanic currents. For example, Michael Faraday had shown that the reaction of an acid liquid with zinc produced a current intense enough to cause the decomposition of potassium iodide (Faraday, 1833). Others had proved that the more a liquid attacked chemically a metal, the more the latter produced electricity, as if electricity was only an effect of the chemical action; a point of view supported by many chemists. Nevertheless, Christian Heinrich Pfaff (1773-1852) had found that if two metals were held under vacuum and in complete absence of water vapor, that is, of whatever body capable of reacting chemically, they became charged with opposite polarity (Pffaf, 1829). In other words, the sole contact of two metals of different nature was enough to produce electricity. Martens described the following experiment, which he believed left no doubt that the simple contact between two heterogeneous bodies, without chemical reaction, was able to develop electricity: into a copper bath, full with acid is submerged a strip of amalgamated zinc (known not to be attacked by acids), without touching the copper. An electric voltage difference is immediately formed between the two metals, stronger than when using ordinary zinc. If wires are soldered to the two poles, a spark will be seen to appear when the two wires come close enough. This voltage difference has developed *before* any chemical action has taken place. Hence, it should be considered as the effect and not the cause (according to Daniel, amalgamated zinc is attacked by acid water but the hydrogen generated attaches to the metal in the form of very small bubbles, and stops the chemical action). Martens quoted a series of additional experiments that proved this assertion, for example, that Davy had reported that a strip of polished zinc in contact with very dry mercury became charged positively. If the strip was hot enough to amalgamate with the mercury, no electrical effect took place. All these experiences showed that the liquid interposed between the metal parts not only served as conductor and as transmitter of the electric fluid, but also to produce an electrical state that added to that resulting of their mutual contact. This reinforced effect seemed to be the principal agent of the electrochemical outcome of the cell and suggested that the maximum effect of a pile would be attained with a liquid that was, at the same time, a good conductor and a powerful excitant of electricity. These arguments explained the common practice of using a liquid phase composed of water mixed with sulfuric or nitric acids. In addition, the electric current ought to be the same everywhere and to exert a uniform chemical action (equally strong). This meant that the chemical decomposition produced by the external current of the cell had to be equivalent to the one produced by the interior one (Martens, 1839c).

In the following section Martens wrote that since during the decomposition of a body by a cell the elements of the substance moved in opposite directions, it was important to determine the direction of the electrical current. The many experiments reported indicated that when a strip of oxidizable metal was submerged in a liquid capable of oxidizing it, the metal became charged positively, while the other pole became charged negatively. Since the most oxidizable metals became charged positively when put in contact with a less oxidizable metal, it was accepted that the electromotive force of metals acted in the same direction as the electromotive force of acid liquid conductors. Martens illustrated these facts with the following experiment: When strips of platinum and zinc are immersed, without touching, in an acid solution, the current is produced only by the action of an acid liquid on the strips. The *submerged* part of the zinc strip will become charged positively while that *above* the liquid will be charged negatively. The electrical current will flow from the zinc to the platinum through an acid solution, and will flow in the opposite direction through a solution of potassium iodide. In the first case, if the two metals are put in contact, the platinum by being less oxidizable will become negative, instead of the non-submerged part of the zinc. In these situations the current will flow from the zinc to the platinum when the solution is of potassium iodide and in the opposite direction when the liquid is acid. Hence, it becomes very simple to determine the direction of the electrical current: in a pile composed of copper and zinc electrodes submerged in an acid conductor, the current will flow from the zinc to the copper (Martens, 1839c).

Martens went on to describe a series of experiments to reinforce the explanations about the mechanism of action of a galvanic cell, and summarized his findings as follows: (a) the development of electricity in galvanic cells must be attributed simultaneously to the metallic contact and the contact of the conducing liquid with the metals of the pile, particularly with the one which oxidizes more easily; (b) the chemical action of the acid conducting fluid over the metals of the pile hardly influences the production of the electrical current. A strong chemical action between two bodies assumes, in general, a large difference between their electrical states, or a strong electromotive action as a consequence of their contact; (c) if the internal chemical action of an active cell is proportional or equivalent to its external chemical action (that is, to the one produced by an external current) it does not mean that one is the cause of the other, but that both are the effect of the same electrical current circulating in the inside and exterior of the cell; (d) the electrical currents produced during the combination of several substances, are probably the result of the electrical states that these bodies assume by contact before they combine; (e) the manner in which the electricity distributes itself in an isolated cell originates from the fact that the electromotive force tends to inscribe to the extreme plates an electrical voltage, which is in inverse ratio to the conductivity of the cell; (f) the electrical state of the different couples connected by a good conductor is distributed equally everywhere; the electricity that flows between the poles originates exclusively from the last plates that constitute the cell; (g) the presence of a large number of couples in a cell does not increase the voltage when the cell is isolated; when it is closed it forces the external current to flow though the poor conductors; (h) the chemical decomposition originated by a cell between the liquid components is the result of a kind of electrical polarity imposed on their molecules in the direction of the current; this polarity causes a mutual exchange of elements among all the molecules located in the trajectory of the current, so that the definite decomposition occurs *only* at the poles of the cell; (i) the transport of the elements of a composed body is only an apparent phenomenon; (j) when the conducting liquid is interrupted every so often by metallic wires, the elements of the compound become free at each end of the wires; and finally, (k) the chemical action of the poles of the cell may influence the decompositions produced by the electrical current; thus, if the poles are prone to oxidation, the decomposition of water can be produced by only one galvanic element, an effect that does not occur in the opposite situation. Here, chemical affinity joins forces with the electrical forces to produce the decomposition (Martens, 1839c).

Azeotropy

In 1847 Martens published a paper describing the phenomena observed when boiling an aqueous solution of HCl (Martens, 1847a). This publication is interesting because it gives an historical view of azeotropy way before this effect received its name. Martens wrote that the aqueous solutions of HCl presented singular variations of composition when they were heated in an open vessel. When boiling a fuming solution of the acid it would became more *dilute* until the liquid would contain between 10 to 20% of the acid, or according to the results of Amand Bineau (1812-1861), just until it became a solution containing 1 equivalent of acid in 16 of water. When distilling a solution containing less than 20% weight of acid, it would become *more* concentrated until it would achieve the value indicated above and continue distilling with constant composition (Bineau, 1842). According to Martens, although these results tempted chemists to assume that the acid obtained under these conditions was a true compound of the acid and water, it was not be because it assumed the existence of acid hydrate formed of one equivalent of acid and 16 of water, a ratio unknown for an acid. Thus it was necessary to look for another explanation.

Some chemists believed that the natural evaporation of aqueous HCl at room temperature would lead to a composition different from the one obtained by boiling. This assumption led Martens to test this possibility. For this purpose he put in a large glass bell 100 cm^3 of an aqueous of HCl containing about 38% weight of the acid and let it evaporate at 10 to 15 ^{0}C. About 2 months later he found that the concentration had decreased to 20.5% weight (as determined by titration with silver nitrate). The same result was obtained when putting the concentrated acid in a closed vessel in the presence of calcium hydroxide (today we know that at atmospheric the system HCl-water presents an azeotrope boiling at 108.6 ^{0}C and containing 20.2% HCl) (Martens, 1847a).

Martens believed that his results agreed very well with the theory that described the formation of vapors from mixtures of liquids having different volatility: An aqueous solution containing 19 to 20% of HCl boiled at 111 ^{0}C when put in a closed glass vessel. Water had lost its volatility by uniting with the acid; the acid liquid had to, by its presence, diminished the vapor pressure of water; the same effect that happened to water in a saline solution boiling at 111 ^{0}C. Hence, water, in a sufficiently humid atmosphere had to condense partially, and become progressively diluted (until equality of the partial pressures). This phenomenon would not take place with an aqueous solution of ammonia, which boiled always at temperatures below 100 ^{0}C. Boiling would lead this solution to lose completely its alkaline component. The aqueous solution of HCl was unable to change its composition beyond 111 ^{0}C because at that temperature it had achieved its minimum volatility (at the azeotropic point the value of the volatility of each component and of the relative volatility is 1, independently if the system presents a maximum or minimum temperature azeotrope. In addition, the identity of the "most volatile component" changes from one section of the boiling point diagram to the other) (Martens, 1847a).

Adulteration of wheat flour

At one time Martens was asked by a judge to test if a certain batch of wheat flour was adulterated with field beans and other foreign substances. This request led him to make a detailed study of the different analytical procedures available for testing adulteration, and to propose a new and better procedure (Martens, 1847b, 1850a, 1852a).

In the initial part of his work Martens found that in order to extract by water maceration the globulin of wheat flour adulterated with field beans, lentils, vetches, etc. it was not necessary to prolong the process for more than 2 hours, because at the end of this time the amount of globulin precipitated by acetic acid begun to decrease and after 12 hours there were no traces of it in the filtrate. This result proved that the globulin was modified by the maceration, and that the rate of this change increased as the temperature went up. His results indicated that it was enough to macerate the suspected flour for 1 to 2 hours, with 3 to 4 times its weight of water, at a temperature below 12 ^{0}C. The filtrated liquid was then treated with acetic acid. According to Martens, even so, the procedure did not extract all the globulin because of its low solubility in water His results indicated that the process was able to extract only about 50% of the globulin present in wheat flour adulterated with 10% of flour of field beans. This yield was not improved by carrying the maceration with water containing about 5% of ammonia, as recommended by some analysts. More than that, Martens claimed that this kind of procedure should never be employed with a flour containing gluten (Martens, 1847b, 1850a, 1852a).

Martens also found that when wheat flour was suspected of containing flour from field beans or from potatoes, as well as mineral substances, it was important to dilute the starch obtained by mechanical analysis in 10 times its weight of water, and filter the mixture after about 20% of the starch had settled down. This first deposit contained the heaviest particles of starch, most of the mineral substances, and the globulin of potato starch. The mineral substances could be easily identified by their physical and chemical properties. A microscopic examination allowed an easy differentiation of the potatoes starch from that of wheat flour, by its volume and shape. Martens added that a chemical reaction discovered by Louis Rene Le Canu (1800-1871) provided an excellent tool for identifying the presence of flour from field beans, vetches, and lentils (Le Canu, 1849): Heating a flour sample with its weight of aqueous HCl led the cellular residue of these impurities to assume a wine color, while that of the flour of wheat, beans, and peas, remained colorless (Martens, 1847b, 1850a, 1852a).

Martens recommended that the use of a two-stage analytical process for the chemical-legal analysis of wheat flour. The first stage consisted of a series of physical operations, which included visual and microscopic description of the flour; detection of the presence of traces of molds, spores of fungi, or ammonium salts; water content, ability to absorb water, distribution of particle sizes, weight of cinders obtained by calcination, etc. The following stage involved maceration and visual and microscopic examination of the resulting globulin, analysis of the filtrate, physical properties of the dough, and chemical tests as described above (Martens, 1847b, 1850a, 1852a).

Plant coloration

Martens published two papers analyzing the phenomena of coloration in plants (Martens, 1853, 1855). In his discussion about the subject, he stated that it was accepted that in the vegetable kingdom only three simple colors were present, the blue, the yellow, and the red, and that with these three colors nature and art produced the infinite variety of colors known. Now, the green color, so widely disseminated in this kingdom, and in all parts of the plant, was not a simple color because the prism decomposed it into blue and yellow. This fact had led to ask if green chlorophyll, instead of constituting a primitive or defined principle, was formed by two dyes, one yellow and one blue, which by their mixture yielded the green hue. It was known that acids caused the blue color to change to red and that the mixing of this blue with red generated the series of tonalities that the botanist had named, after August Pyrame de Candolle (1778-1841), the *cyanic series* (Le Candolle, 1829). This series was easily reproduced in the laboratory by adding acid progressively to the coloring matter until it converted totally into red. In the same manner it was possible to imitate the *xanthic series* by adding progressively to yellow a red colored substance. Martens mentioned that it was probable that nature operated in the same manner (taking into account that it was possible to produce mixed colored by superposition of substances colored differently). Now, all the red color substances present in plants did not necessarily originate from blue ones being changed by an acid. They could originate from yellow by oxygenation, as did the red from the xanthic series. Alkalis did not change this red to blue; they changed it to yellow. Further addition of an acid reestablished the original red color. This red color present in the leaves was far from being always the same; it constituted what was called an *erytrophyll substance*. The red color developed in many leaves during the autumn belonged, generally, to the cyanic series, while the red assumed by certain leaves in winter belonged to the xanthic series. The color changes that occurred in leaves also took place in flowers. It was generally accepted that the red of the cyanic series was more soluble in water than that of the xanthic series (Martens, 1853).

According to Martens, all the coloring phenomena taking place in leaves could be easily explained by admitting that chlorophyll contained two different coloring substances, one blue and the other yellow, and that these could form separately in different cells. The changes in tint that took place in the green parts of plants during the different stages of its life could be thus attributed to changes in the proportion in which the blue and the yellow were associated in chlorophyll. The yellow color presented by autumn leaves (xanthophylls) was present formed in the chlorophyll. The xanthophylls had all the solubility characteristics of chlorophyll, they were soluble in alcohol and ether, insoluble in water, and were always associated with a fatty substance (Martens, 1853).

Martens described the experiments he had conducted with a large variety of leaves and flowers (*Eranthemun strictum*, narcissus, camellia, chrysanthemum, hortensia, begonia, etc) to separate these two colors, and then listed his conclusions: (a) the only two fundamental colors present in plants were the blue and the yellow (anthocyanine and anthoxantine); (b) these fundamental colors formed in the petals and in the herbal parts; (c) chlorophyll tended always to become yellow due to the great instability of the blue colorant, unless the latter had been stabilized by its combination with an acid that turned it red. In this situation, the leaves, instead of becoming yellow because of the alteration of the chlorophyll, assumed a red color; (d) the red color present in the leaves was not always caused by the presence of an acid; it could have originated from the oxygenation of the xanthophylls; (e) the yellow and blue coloring substances were probably transported to the surface of the plant by the phenomenon of aqueous transpiration; and finally, (f) the red color of both series (cyanic and xanthic) did not necessarily had to be the same substance. The red of the xanthic series was more common in flowers than in the leaves (Martens, 1853).

In the following paper, Martens reported that Edouard Filhol (1814-1883) had recently reported that all white flowers contained a colored principle, which turned yellow in contact with alkalis. Hence it was possible to turn yellow a white flower by exposing it to ammonia (Filhol, 1854; Martens, 1855). Martens repeated the Filhol's experiences and found that this phenomenon was much more general than reported: The yellow coloring substance was located in all the superficial or sub-epidermis parts of the plant. Martens went on to describe the experimental techniques he had used to separate this principle from flowers, leaves, and plant juice. He experimented with the yellow substance obtained from a large variety of plants, and reached the following conclusion: (a) all plants elaborated within the cells of their sub-epidermis parenchyma a pale yellow juice that tended to become deep yellow by oxygenation by means of alkalis or sunlight; (b) this coloring principle was modified in a variety of manners by the act of vegetation, or by association with fatty materials, which turned it insoluble, and gave place to the gamma of yellow colors present in leaves and flowers. These colors could turn red under the prolonged influence of light and oxygen; (c) the same extractive principle, known as xanthein, coexisted in the plant along other coloring substances, particularly with the blue principle or antocyane; and (d) the colors of the cyanic series were usually accompanied in the flowers by xanthic colors (Martens, 1855).

***Figure 1**: Martin Martens (1797-1863)*

BIBLIOGRAPHIC REFERENCES

Balard, A. J. (1834). Recherches sur la Nature des Combinaisons Décolorants du Chlore. *J. Pharm., 20*, 661- 674.

Bineau, A. (1842). Recherches sur les Combinaisons de l'Eau avec les Hydracides. *Compt. Rendus*, *15*, 775-777.

De Candolle, A. P. (1829). Sur le Changement de Couleur des Fleurs d'Hibiscus Mutabilis. *Bib. Univers.*, *41*, 83-84, 1829.

Faraday, M. (1833). Experimental Researches on Electricity. Fifth Series. On Electro-chemical Decomposition. *Phil. Trans.*, 675-710.

Filhol, E. (1854). Observations sur les Matières Colorantes de Fleurs. *Compt. Rendus*, *39*, 194-198.

Gay-Lussac, J. L. (1842). Sur les Combinaisons du Chlore avec les Bases. *Compt. Rendus*, *14*, 927-952, 1842; *Ann. Chim. Phys.* [3], *5*, 273-304.

Le Canu, L. R. (1849). Des Falsification des Farines. *J. Pharm.*, *15*, 241-258.

Liebig, J. (1832). Sur la Préparation de Chlorate de Potasse *Ann. Chim. Phys.49*, 300-302.

Martens, M. (1835a). De l'Affinité et de la Composition Moléculaire des Corps *Bull. Acad. Sci. Bruxelles*, *2*, 179-182.

Martens, M. (1835b). Mémoire sur les Chlorures d'Oxides. *Mém. Couronné, Acad. Roy. Sci., Bruxelles*, *10*, 3-77.

Martens, M. (1836). Mémoire sur les Composes Décolorants Formes par le Chlore. *Bull. Acad. Sci. Bruxelles*, *3*, 188-191; *Ann. Chim. Phys.* 61, 293-319.

Martens, M. (1837a). Notice les Caractères Chimiques des Chlorures de Soufre. *Bull. Acad. Sci. Bruxelles*, *4*, 84-94.

Martens, M. (1837b). Esquisse d'une Nouvelle Classification Chimique des Corps. *Bull. Acad. Sci. Bruxelles*, *4*, 397-410.

Martens, M. (1837c). Réflexions sur la Théorie Electrochimique de l'Affinité et la Composition Moléculaire des Corps. *Mém. Acad. Sci. Bruxelles*, *10*, 1837; published as booklet by Hayez, Bruxelles.

Martens, M. (1839a). De l'Influence de la Cohésion sur les Réactions Chimiques. *Bull. Acad. Sci. Bruxelles*, *6*(2), 49-65.

Martens, M. (1839b). De l'Influence de la Masse des Corps sur les Réactions Chimiques. *Bull. Acad. Sci. Bruxelles*, *6*(2), 149-161.

Martens, M. (1839c). Mémoire sur la Pile Galvanique, et sur la Manière dont elle Opère les Décompositions des Corps. *Mém. Acad. Sci. Bruxelles*, *12*, 1839 (47 pages); published as booklet by Hayez, Bruxelles.

Martens, M. (1842a). Recherches sur les Causes Productrices de la Passivité des Métaux. *Bull. Acad. Sci. Bruxelles*, *9*(2), 527-546.

Martens, M. (1842b). Sur les Causes Combinaisons du Chlore avec les Bases. *Bull. Acad. Sci. Bruxelles*, *9*(2), 180-192.

Martens, M. (1842c). Notice sur la Théorie de la Pile Voltaïque. *Bull. Acad. Sci. Bruxelles*, *9*(2), 192-202.

Martens, M. (1843a). Note sur les Combinaisons du Chlore avec les Oxydes Alcalins. *Bull. Acad. Sci. Bruxelles*, *10*(1) 103-110.

Martens, M. (1843b). Note sur la Passivité des Métaux. *Bull. Acad. Sci. Bruxelles*, *10*(2), 406-414.

Martens, M. (1844). Mémoire sur les Composes Décolorants Formés par le Chlore avec les Oxydes Alcalins. *Mém. Acad. Sci. Bruxelles*, *17* (63 pages).

Martens, M. (1845). Recherches sur la Force Electromotrice du Fer. *Bull. Acad. Sci. Bruxelles*, *7*, 393-406, 1845; published as booklet by Hayez, Bruxelles.

Martens, M. (1847a). Note sur la Constitution de l'Acide Chlorhydrique Liquide. *Bull. Acad. Sci. Bruxelles*, *14*(1), 441-448.

Martens, M. (1847b). Sur les Falsifications de la Farine. *Bull. Acad. Sci. Bruxelles*, *14*(2), 60-62.

Martens, M. (1850a). Remarques sur la Recherche des Falsifications des Farines. *Bull. Acad. Sci. Bruxelles*, *17*(1), 197-216.

Martens, M. (1850b). De la Théorie Electrochimique dans ses Rapports avec la Loi des Substitutions. *Bull. Acad. Sci. Bruxelles*,*17*(2), 388-404.

Martens, M. (1851). Sur les Piles à Acides et Alcalis, Séparés par des Corps Poreux. *Bull. Acad. Sci. Bruxelles*, *18*(2), 14-17.

Martens, M. (1852a). Note sur la Falsifications des Farines. *Bull. Acad. Sci. Bruxelles*, *19*(2), 323-330.

Martens, M. (1852b). Sur les Décompositions Électro-Chimiques. *Bull. Acad. Sci. Bruxelles*, *19*(3), 302-314.

Martens, M. (1853). Recherches sur les Couleurs des Végétaux. *Bull. Acad. Sci. Bruxelles*, *20*, 197-234.

Martens, M. (1854). Sur l'Origine ou la Nature du Calorique. *Bull. Acad. Sci. Bruxelles*,*21*, 149-159.

Martens, M. (1855). Nouvelles Recherches sur la Coloration des Plantes. *Bull. Acad. Sci. Bruxelles*,*22*, 157-179.

Martens, M. (1861). Considérations sur la Nature of Simple Bodies. *Bull. Acad. Sci. Bruxelles*, *11*, 193-199.

Martens, M. (1862). Sur l'Origine de l'Électricité dans les Piles. *Bull. Acad. Sci. Bruxelles*, *13*, 36-44.

Martens, M. & Galeotti H. (1842). Mémoire sur les Fougères du Mexique, et Considérations sur la Géographie Botanique de cette Contrée. *Mém. Acad. Sci. Bruxelles, 15*; published as booklet by Hayez, Bruxelles.

Martens, M. & Galeotti H. G. (1842-1845) Enumeratio Synoptica Plantarum Phanerogamicarum ab Henrico Galeotti in Regionious Mexicanis Collectarum. *Mém. Acad. Roy. Bruxelles*, *9*, 32-46, 227-249, 372-393, 1842; *10*, 31-52, 110-134, 178-200, 208-225, 302-321, 341-360, 1843; *11*, 121-137, 227-243, 355-376, 1844; *12*, 129-149, 1845.

Pffaf, C. H. (1829). Défense de la Théorie de Volta, Relative à la Production de l'Électricité par le Simple Contact, Contre le Objections de M. de la Rive. *Ann. Chim. Phys.*, *41*, 236-247.

Pire, L. (1863). Notice Nécrologique sur M. Martin Martens. *Soc. Roy. Botan. Belgique*, *2*, 67-71.