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ANDRÉS MANUEL DEL RIO, DISCOVERER OF VANADIUM

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ABSTRACT

Andrés Manuel Del Rio was born in Madrid in 1764 and died in Mexico City in 1849. He studied mineralogy, geology, metallurgy and mining engineering at the Royal Academy of Mines of Almadén and the Patriotic Seminary of Vergara. In 1871, with a stipend from the Spanish Crown, he continued his studies in Paris, Freiberg, Chemnitz and other scientific centers throughout Europe, particularly in metallurgy. In 1794 at the invitation of Don Fausto Delhuyar, who together with his brother Juan José Delhuyar discovered tungsten in 1783, Andrés Manuel Del Rio went to Mexico where he was professor at the School of Mines for more than fifty years, until his death. In 1801, while analyzing a lead mineral from Zimpán, Hidalgo, Mexico, he discovered a new element that he called panchromium or eryhtronium, because of the red colors, characteristic of its salts. In 1831, the Swedish chemist Nils Gabriel Serfström rediscovered erythronium in an iron ore from Taberg, Småland, Sweden and named it vanadium in honor of the Scandinavian goddess Vanadis.

RESUMO

Andrés Manuel Del Rio nasceu em Madrid em 1764 e morreu na Cidade do México em 1849. Estudou mineralogia, geologia, metalurgia e engenharia de minas na Real Academia de Minas de Almadén e no Seminário Patriótico de Vergara. Em 1781, com uma bolsa de estudos da Coroa Espanhola, viajou para Paris, Freiberg, Chemnitz e outros centros metalúrgicos da Europa para trabalhos de especialização. A pedido de Don Fausto Delhuyar, que junto com o seu irmão Juan José descobriu o tungstênio em Vergara em 1781, Andrés Manuel Del Rio foi para México a ocupar o cargo de professor na Escola de Minas onde trabalhou por mais de cinquenta anos, até a sua morte. Em 1801, enquanto analisava um minério de chumbo de Zimpán, Hidalgo, México, descobriu o elemento que ele chamou de pancromo ou eritrônio, devido as cores vermelhas, características de seus sais. Em 1831, o químico sueco Nils Gabriel Serfström redescobriu o eritrônio num minério de ferro proveniente de Taberg, Småland, Suécia e o chamou de vanádio em homenagem à deusa escandinava Vanádia.

KEYWORDS History of Chemistry, Vanadium, Erythronium, Panchromium, Discovery of the Elements.

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Contrary to general belief in certain circles, many scientists that were born, lived or worked in Latin America, made important contributions to chemistry. Among them are Bartolomé de Medina who set up amalgamation as an industrial process; Antonio De Ulloa, who was the first to take platinum to Europe; Fausto and Juan José Delhuyar, discoverers of tungsten; Andrés Manuel Del Rio, discoverer of vanadium; José Luis Casaseca, founder of the Cuban Institute of Chemical Research in 1848; Alvaro Reynoso, father of modern sugar technology and Luis Frederico Leloir, Nobel laureate in chemistry. Significant contributions were also made by Horácio Damianovich in noble gas chenistry, Gustavo Fester, Xorge Alejandro Dominguez and Otto Gottlieb in natural products and Ernesto Giesbrecht in the chemistry of lanthanides.[1-14] In 1995 the Mexican chemist Mario Molina was awarded the Nobel Prize in Chemistry together with Paul Crutzen and F. Sherwood Rowland for their work on the ozone layer.

Andrés Manuel Del Rio was born in Madrid on November 10, 1764 and passed away in Mexico City on March 23, 1849. He studied mineralogy, geology, metallurgy and mining engineering at the Royal Academy of Mines of Almadén and the Patriotic Seminary of Vergara. It was at the School of Mines of Vergara that Fausto and Juan José Delhuyar discovered tungsten or wolfram in 1783.

After completing studies in Spain, Del Rio received a stipend from the Spanish Crown and in 1781 travelled to Paris and later Freiberg, Chemnitz (Schemnitz) and other scientific centers throughout Europe. He returned to Spain, more than a decade later, in 1793. In Paris, he studied chemistry with Darcet and acquired experience in porcelain and ceramics manufacturing and processing. In Chemnitz, Freiberg and various metallurgic centers in France, England and other European countries, Del Rio specialized in metallurgy and mining engineering. While in Freiberg, he was a devoted student of Abraham Gottlob Werner and became fascinated by mineralogy.

Soon after his return to Spain, at the invitation of Don Fausto Delhuyar, Andrés Manuel Del Rio went to Mexico where he was appointed professor at the School of Mines (*Colegio de Minería*). He arrived in Mexico on December 18, 1794. There he lived and worked, with few interruptions, for almost half a century, until his death in 1849.

From 1820 to 1823 he represented Mexico as a deputy in the Spanish Cortes and from 1829 to 1832 he lived in exile in Philadelphia, United States. In 1820 he pleaded for Mexico's independence in the Cortes and in 1829, when the Mexican Government expelled the Spanish (although he was not included among them) he went to exile in Philadelphia, in solidarity with his fellow countrymen.

At the Colegio de Minería (School of Mines), Del Rio taught mineralogy, French, geology, mining engineering and metallurgy. He wrote many textbooks including *Arte de las Minas*,

Geometria Subterránea, Tratado de Vetas (Treatise on Lodes or Mineral Veins) and *Elementos de Orictognosia* (Elements of Fossil Science and Mineralogy). He also translated various manuals including the *New Mineral System of Berzelius*, a *Textbook of Geology*, extracted from *Lethae Geognosticae* by Bronn and annotaed, translated and commented Karsten's Mineralogical Tables (*Tablas Mineralogicas de Karsten*).

Elementos de Orictognosia, by far the most important work, was first published in two volumes in Mexico in 1795 and 1805. The second expanded edition was divided into two parts, practical and theoretical. The practical part, that Del Rio considered more important and included the description of many minerals from Mexico, was published in Philadelphia in in 1832 during his exile in the United States. The second or theoretical part was published after his return to Mexico and a thorough revision in 1846. Alexander von Humboldt said that it was the best book on mineralogy in Spanish and Guyton de Morveau considered it the best book on minearlogy in all languages.[11,15]

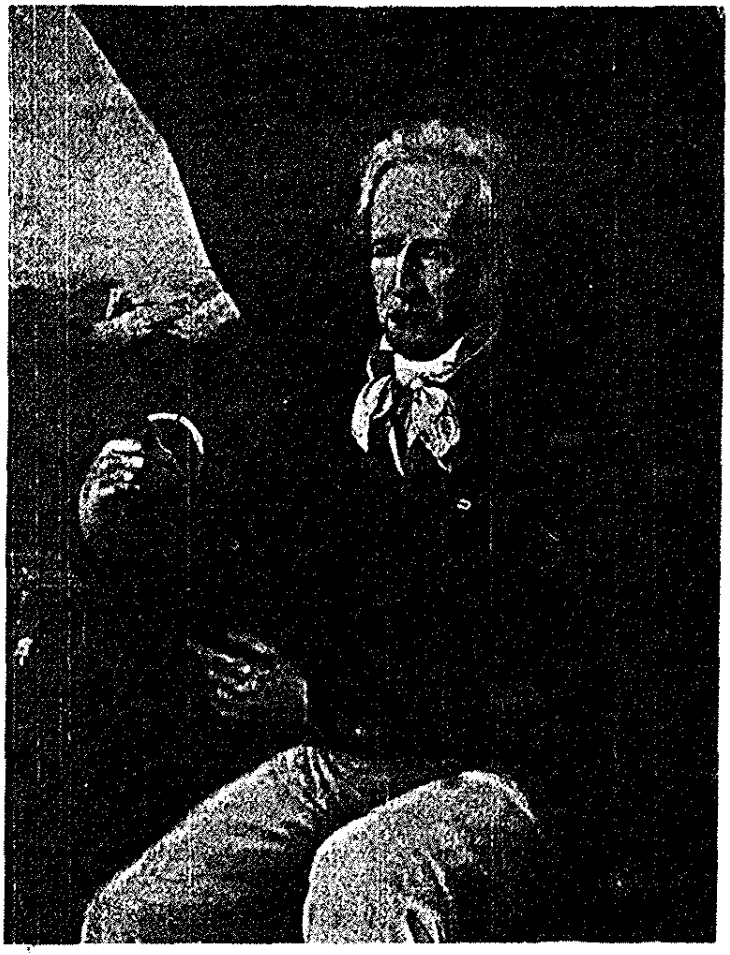
On the more practical side, Del Rio developed a pump for draining water from mines, was the manager of the first formal iron and steel foundry of Latin America in Coalcomán, Michoacán, Mexico from 1805 to 1809, director of the Casa de Moneda (Public Mint), deputy in the Mining Tribunal and honorary councilman of Mexico City.

His main research interest was the study of minerals found in Mexico and in particular of vanadinite, $PbCl_2 \cdot 3Pb_3(VO_4)_2$. He published a large number of papers dealing with minerals and geology in the main European journals and also in scientific periodicals from Mexico and the United States.

It was in 1801, while analyzing the grey lead mineral vanadinite from Zimpán, Hidalgo, Mexico that Andrés Manuel Del Rio discovered a new element that he at first called *panchromium*, beacuse of the many colors of its oxides and later *erythronium*, because of the characteristic red colors of its salts. On September 26, 1802 he communicated his discovery to Don Antonio Cabanilles (Cavanilles), who published it in the *Anales de Ciencias Naturales de Madrid* in May of 1803 (volume VI, Number 16).[16-18]

The discovery, as described by Del Rio himself in a footnote on page 61 of *Tablas Mineralogicas de Karsten* published in 1804 is given below,[11,16]

> "Habiendo destilado tres o cuatro veces media onza (de la mena de Zimapán)en polvo con ácido sulfúrico diluido y lavado el residuo a cada vez, tuve una disolución verde, que saturada con exceso de amonia me dio a los pocos días costras compuestas de agujas en la superficie del líquido o estrellitas compuestas de pirámides muy agudas en las paredes de la copilla. Estos cristalitos, que eran blancos, lavados en muy poca agua, porque se disuelven en frío y secados al aire libre, tomaron el más bello roxo de escarlata inmediatamente que tocaron una sola gota de ácido concentrado; quando estaba diluido, se ponían primero amarillos y luego roxos. Estos ácidos los disolvía sin descomponerlos. Lo mismo sucedió con la potasa, la sosa, la cal, etc., excepto que los



ANDRÉS MANUEL DEL RIO (1764-1849),
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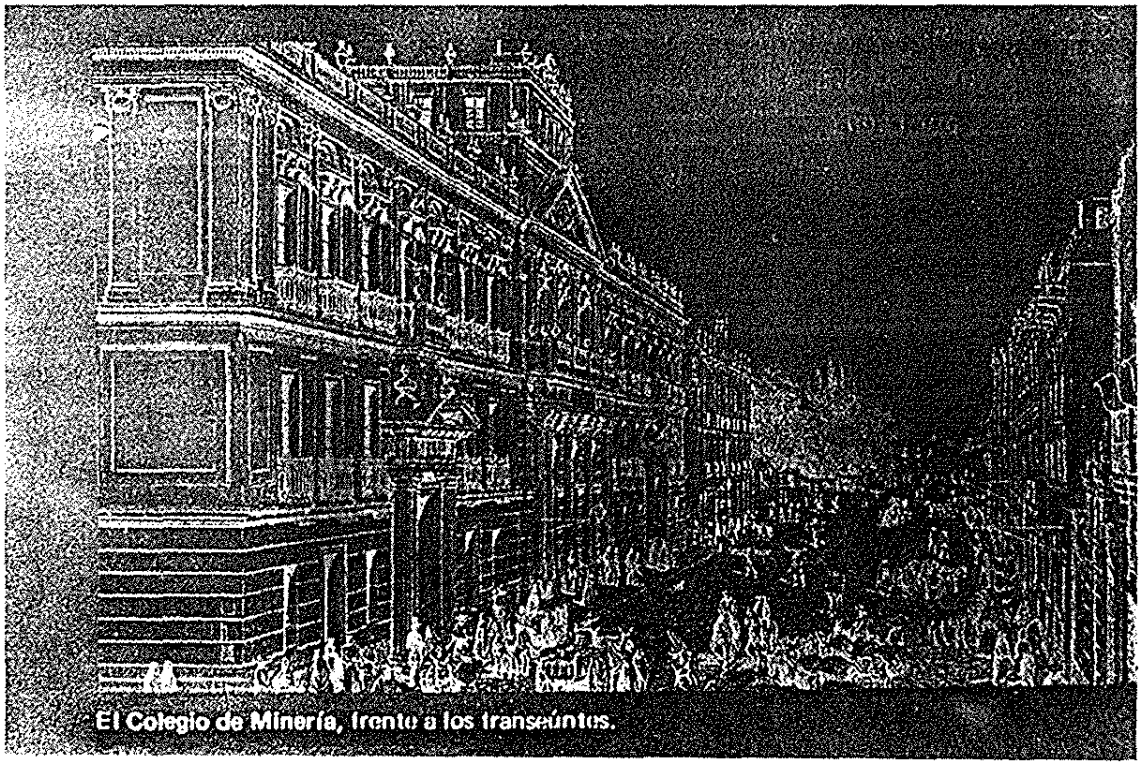

THE SCHOOL OF MINES OF MEXICO IN AN ENGRAVING OF THE TIME.

rombitos que dio la potasa solo se volvieron amarillos. Saturando el exceso de amonia con ácido nítrico, y concentrado un poco por evaporación, obtuve despues prismitas de sabor algo punzante y metálico y de un bello roxo de aurora, qu parecían quadrangulares rectángulos apuntados con cuatro caras puestas sobre las aristas. Haciendo lo mismo con la sosa, me dio cristalitos roxos de aurora, que parecían tablas quadrangulares oblicuángulas, y con la potasa, tablitas quadrangulares rectángulas amarillas. Poniendo 17,75 granos de las agujas formadas por la amonia baxo la mufla de un tiesto de porcelana, tomaron el más bello roxo, sin perder su figura, y luego se fundieron en una masa opaca de color entre pardo de hígado y gris plomo, con muy finas estrellitas en la superficie de lustre semimetálico, que pesó 11,75 granos. No sufrió alteración alguna al fuego de la fragua en hora y media que se tuvo en un crisolito con carbón; es verdad que la cantidad era muy poca; solo la materia ennegrecida con el carbón y con 1,25 granos de aumento. Se metió en una retorta con ácido nítrico; hubo vapores roxos al fin, y la susbstancia se puso roxa; se repitió dos veces lo mismo; se aumentó al fin al fuego para desprender todo ácido, y echando agua fría se volvió emulsiva. Aclarada la emulsión con el tiempo, no enroxecía la tintura de rábano, aunque daba precipitados amarillos con disoluciones nítricas de plata, mercurio y plomo, no con la muriática del último; precipitaba verde esmeralda el prusiato calizo, y ponía verde oscura la tintura de agallas. El sedimento verde aceituna que se había formado se puso roxo instantáneamente con un poco de ácido nítrico, y la disolución amarillenta precipitaba un óxido verde con el zinc y el hierro. Al soplete con borax tomaba también el vidrio un color verde hierba. La proporción de las partes por quintal de plomo pardo es de 80,72 de óxido amarillo de plomo y de 14,80 de esta nueva substancia (eritronio), siendo por lo demás un poco de arsénico, óxido de hierro y ácido muriático. Su combinación con la amonia no se amalgamó con el mercurio. Pareciéndome nueva esta substancia, la llamé pancromo por la universalidad de colores de sus óxidos, disoluciones, sales y precipitados, y después *eritronio* por formar con los álcalis y las tierras sales que se ponían roxas al fuego y con los ácidos"

As can be seen from the description above, Del Rio did a series of exhaustive analyses and had no doubt that he had discovered a new substance. During Baron Alexander von Humboldt's visit to Mexico, Del Rio also communicated to him the discovery of the new element. Von Humboldt, for his own reasons,believed that the new element was chromium. Upon his departure from Mexico, Del Rio, who considered von Humboltd a friend, gave him a sample of the brownish-gray lead mineral from Zimpān as well as a copy in French describing the discovery. As Del Rio stated in 1832 (See *Elementos de Orictognosia*, 2nd edition, J. F. Hurtel, Philadeplphia, 1832, pp. 484-485), von Humboldt did not even bother to show a copy the experiments to H.V. Collet-Descotils,[19] a renowned French analytical chemist, who identified the mineral as lead chromate. Del Rio was forced to admit that he was mistaken and that the mineral from Zimpān contained 80.72% lead oxide and 14.80% chromic acid.

In 1831 the Swedish chemist Nils Gabriel Serfström, working in Berzelius's laboratory rediscovered erythronium in an iron ore from Taberg, Småland, Sweden and named it vanadium in honor of the Scandinavian goddess Vanadis.

Soon afterwards, F. Wöhler also discovered vanadium in a sample of the mineral from Zimpán given to him by Baron A. von Humboldt and proved that Del Rio was correct in his original analysis. It is interesting to read the correspondence between Berzelius and Wöhler and the latter's lines to Liebig. They offer some astonishing clues about the side-scenes and the development of science.[20] Be it as it may, the discovery of vanadium can be considered an outstanding accomplishment for science in Mexico and Latin America. The next discovery of an element in a laboratory of the United States took place almost one and a quarter century later.

Andrés Manuel Del Rio's more than fifty years of service to science in Mexico has been duly recognized. The highest prize awarded by the Mexican Chemical Society bears his name.

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