



Edmund Davy

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Abstract

Edmund Davy (1785-1857) was a British scientist to whom we owe the discovery of acetylene (by accident), potassium carbide, the platinum sponge, the synthesis of a variety of new platinum compounds, and an electrochemical procedure for determining small amounts of platinum. He carried an extensive research on platinum and its derivatives; in particular, he studied the reaction of platinum with hydrogen sulfide, oxygen, chlorine, and phosphine, the preparation and properties of simple salts of platinum such as platinum sulfate, and the triple salts of platinum with potassium, sodium, ammonium, aluminum, and barium. Davy also studied the preparation and properties of the fulminates of platinum and silver, and developed a new electrochemical analytical procedure for detecting the presence of arsenic(II) and arsenic(III) oxides.

Keywords

acetylene, arsenic, platinum and derivatives, potassium carbide.

Resumen

Edmund Davy (1785-1857), un científico inglés a quien le debemos el descubrimiento del acetileno (por accidente), el carburo de potasio, la esponja de platino, la síntesis de nuevos compuestos del platino, y un método electroquímico para detectar cantidades mínimas de arsénico. Estudio extensamente el platino y sus derivados, en particular, su reacción con el ácido sulfhídrico, oxígeno, cloro y la fosfina, la preparación y propiedades de sales simples como el sulfato de platino, y las sales triples del platino con potasio, sodio, amoníaco, aluminio y bario. Davy también estudió la preparación y propiedades de los fulminatos de platino y plata y desarrolló un nuevo proceso de análisis electroquímico para detectar la presencia de los óxidos de arsénico(II) y arsénico(III).

Palabras clave

acetileno, arsénico, carburo de potasio, platino y derivados.

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Life and career (Barker, 1856-1857; Russell, 1954; Lindsey, 2016)

Edmund Davy, born in 1785 at Penzance, Cornwall, England, was the second son of William Davy, a curator. In 1804, after finishing his basic education in Penzance, he moved to London where he worked for eight years as operator and assistant in the laboratory of his cousin Humphry Davy (1778-1829) in the Royal Institution of London. During this period he also held the position of superintendent of the mineralogical collection of the Royal Society of London. In 1813 he was elected professor of chemistry in the Royal Cork Institution, a well-known organization devoted to the promotion and popularization of practical science. After 13 years in this position he moved to the Royal Dublin Society as professor of chemistry. Sometime afterwards he was elected fellow of the Royal Society of London and of the Chemical Society of London, member of the Royal Irish Academy, and honorary member of the Société Française de Statistique Universelle.

Davy passed away on November 5, 1857, in Kimmage, Dublin. According to Lindsey he was probably buried in St Mary's churchyard, Crumlin (a suburb of Dublin) (Lindsey, 2016).

Scientific contribution

Davy wrote 33 papers on the subjects of inorganic and organic chemistry, mineralogy, and agriculture. In addition to the subjects described below, Davy also studied a species of graphite from Africa (Davy, 1812b); the use of magnesium carbonate to improve the quality of flour and bread (Davy, 1816, 1817bc); the state of air in hospitals (Davy, 1817d); the softening of river water (Davy, 1818); the presence of uric acid in the excrement of the boa constrictor (Davy, 1819); the action of iodine on volatile and fixed oils (Davy, 1822); the synthesis of the new gas chloronitrous acid (Davy, 1831b); galvanic protection (Davy, 1835ab); tobacco and nicotine (Davy, 1835cd); the manufacture of sulfuric acid (Davy, 1850a); the manufacture of solid manure from urine (Davy, 1855); the deodorizing power of miscellaneous substances (Davy, 1856-1857ac); the use of platinum instead of porcelain or glass in March's method (Davy, 1856-1857d); the preparation of gutta-percha based cements (Davy, 1856-1857e); etc.

Platinum and its derivatives

Davy carried on extensive research on platinum and its derivatives (Davy, 1812a). In his first publication he mentioned that the crude ore of platinum had been well investigated but not so the combinations of the metal with inflammable bodies, oxygen, and acids. No one had yet succeeded in uniting platinum with sulfur or phosphorus or in finding these combinations in nature; the early attempts were based on the fact that many metals were able to form sulfides by simply heating their mixture with sulfur or by adding sulfur to the metal heated to redness at atmospheric pressure (Davy, 1812a).

Davy reported that the sulfides could be readily made by heating a mixture of platinum ammonium chloride [today, ammonium hexachloroplatinate (IV)] with sulfur or by exposing under vacuum a mixture of platinum and sulfur to an elevated temperature (Davy, 1812a). In the first procedure the metal in a highly divided state was put in contact with a volatile salt, and in the second, the volatility of the sulfur would be counteracted and the reagents subjected to a high temperature not achievable at atmospheric pressure. Davy prepared the platinum ammonium chloride by heating a strong acid solution of purified platinum with ammonium chloride. The resulting yellow precipitate was washed with distilled water and then dried for some days in a sand bath at a temperature between

93° and 171 °C. The resulting salt contained 44.5% platinum by weight (today, 43.97%). The platinum metal was obtained by decomposing this salt by heating it to redness (about 525 °C) in a platinum crucible. According to Davy the sulfides prepared by these two methods contained different amounts of sulfur and seem to exhibit dissimilar properties (Davy, 1812a).

The super-sulfide of platinum was prepared by heating at dull red (about 700 °C) a 3:2 mixture of ammonium hexachloroplatinate (IV) with sulfur flowers until it stopped releasing gases. According to Davy this sulfide was present as a gray to black powder or small lumps, loosely together, soft to the touch, non conductor of electricity, unaffected by air or by water, scarcely attacked by mineral acids or by a boiling solution of KOH, partially decomposed by fused alkali and by iron filings, and strongly decomposed by heating with KCl and with fine zinc filings. The salt did not decompose when heated to red in an evacuated vessel; in contact with air it decomposed partially at moderate heat and totally at dull red. Davy estimated that the salt contained, by weight, 72% platinum and 28% sulfur [today: platinum (IV) sulfide contains 75.259% Pt and 24. 741% S] (Davy, 1812a).

The sub-sulfide of platinum was prepared by heating to red, in an evacuated tube, a mixture of equal weights of platinum and sulfur. The resulting material was a bluish gray powder or mixture of small particles, having no smell or taste, and a relative density about 6.2. It did not conduct electricity, was not affected by exposure to the atmosphere or to water, and its chemical properties were very similar to those of the super-sulfide. Elemental analysis indicated that it contained, by weight, 84% platinum and 16% of sulfur [today: platinum (II) sulfide contains 85.88% Pt and 14.22% S] (Davy, 1812a).

Davy wrote that two memoirs published by Bernard Pelletier (1761-1797) about the reaction of phosphorus with metals contained most of what was known about the action of phosphorus on platinum (Pelletier, 1789, 1792), and that he believed that Pelletier's experimental methods were far from being acceptable. Pelletier had heated a mixture of 28.35 g of platina, 28.35 g of phosphoric glass, and 1,76 g of powdered charcoal in a crucible for one hour at a temperature high enough to melt gold (1064 °C). After breaking the crucible he had found a small silver white button weighing more than 28 g, accompanied by well-defined crystals of the same substance, shaped as a perfect cube. The resulting platinum phosphuret (phosphide) was quite hard and brittle and heated to fusion it decomposed releasing phosphorus while burning on its surface. Pelletier reported that platinum phosphide detonated strongly when thrown on fused potassium nitrate. A mixture of platinum phosphide and potassium chloride thrown into a red-hot crucible produced a brisk detonation, leaving a residue of pure platinum in the crucible (Pelletier, 1789, 1792).

Davy wrote that platinum and phosphorus combined very easily when heated to a red heat. Heating the phosphide to red heat resulted in partial decomposition with phosphorus being expelled. The compound was completely decomposed at higher temperatures. Davy prepared platinum phosphide using the two methods he had used to prepare platinum sulfide. Once again he found that the two phosphides contained different amounts of sulfur and had different properties (Davy, 1812a). The super-phosphide had similar physical and chemical properties to those of phosphorus sulfide. It appeared as an iron black or grey black powder or small pieces loosely aggregated, exhibiting no smell or taste, and having relative density 5.28. It was not affected by air or water, did not conduct electricity and was little affected by mineral acids and hot fine zinc filings. It was partially decomposed when heated with potassium chloride, releasing oxygen and chlorine. Elemental analysis indicated that it contained, by weight, 70% platinum and 30% phosphorus. Platinum sub-phosphide was a lead gray or bluish gray solid, obtainable

in small porous masses or imperfectly fused and crystallized particles, exhibiting no taste or smell, and having relative density 6. It did not conduct electricity and partially decomposed when heated with potassium chloride. Elemental analysis indicated that it contained, by weight, 82.5% platinum and 17.5% phosphorus (Davy, 1812a).

Davy also studied the reaction of platinum with hydrogen sulfide, oxygen, and chlorine, of platinum chloride with phosphine, and the properties of simple salts of platinum such as platinum sulfate, the potassium, sodium, ammonium, aluminum, and barium sulfates of platinum, and of fulminating platinum (Davy, 1812c). The sulfide derivative was obtained by reacting platinum with a saturated aqueous solution of hydrogen sulfide or by passing a current of the gas through platinum submerged in water. After some time the surface of the metal became covered with a dark gray layer of the product while some of it was also precipitated. Davy described the sulfide as a loose mixture of gray particles having no luster and smell, and an acid taste. Heated below red it deflagrated releasing copious sulfur dioxide fumes and leaving a residue of pure platinum. It showed no reaction with boiling HCl, nitric acid, and aqua regia but decomposed readily when heated with KCl. In contact with air it generated sulfuric acid. Elemental analysis indicated that it contained, by weight, 85% platinum and 15% sulfur. Additional determination of the physical and chemical properties of the compound led Davy to conclude that this material should not be considered a true sulfide of platinum but very possibly a mixture of platinum sulfide and hydrogen sulfide, or of platinum, sulfur, and hydrogen. The presence of hydrogen sulfide was justified by the production of sulfuric acid when in contact with air. Davy also reported that bubbling phosphine through a mixture of water and platinum caused the partial decomposition of the gas at the surface of the liquid, which resulted in a loss of its property of spontaneous inflammation. The globules were delayed at the surface of the fluid and arranged themselves in the form of a honeycomb. Eventually a yellow substance deposited that promptly turned gray (Davy, 1812c).

Davy wrote that the usual methods for preparing the oxides of common metals did not work with platinum, probably because of its ability of forming triple compounds with the alkaline earths, chlorine, and HCl. He reported that he had also been unsuccessful in obtaining the oxide in spite of the many different procedures he had tried for this purpose. He also remarked that platinum seemed to form two distinct compounds with chlorine, one soluble in water and highly deliquescent, and the other insoluble in water. He believed that the soluble form was actually an impure substance, which could be prepared by evaporating to dryness a solution of platinum chloride or precipitated from the solution with chlorargyrite (the mineral form of silver chloride). Davy prepared the insoluble chloride by a lengthy procedure, which involved boiling platinum with HCl, adding occasionally a little nitric acid, evaporating the solution to dryness, treating the residue with HCl, evaporating the acid, heating the new residue to redness, and finally boiling it with a large excess of water. The resulting compound had a dull olive brown or green color, no smell or taste, it was not affected by the atmosphere, was nearly insoluble in water, and heated red it decomposed into chlorine and pure platinum. The chloride was slightly soluble in diluted HCl, concentrated aqua regia, alcohol, and ether. It was insoluble in nitric, sulfuric, phosphoric, and acetic acids at all temperatures. Elemental analysis indicated that it contained, by weight, 72.5% platinum and 2.5% chlorine (Davy, 1812c).

Davy prepared platinum sulfate by reacting washed platinum sulfide with strong nitric acid. The initial reaction was exothermic and resulted in the decomposition of the acid and formation of sulfuric acid. The mixture was then heated until no more nitrous gas was released, and then the material evaporated to dryness. Davy described the resulting platinum sulfate as a very dark, almost black solid, shaped as a porous brittle, brilliant, and very deliquescent cake, and tasting acid. The dry sulfate was soluble in water, ether, HCl, nitric acid, and phosphoric

acids. When boiled to dryness in HCl it released the sulfuric acid leaving an insoluble residue composed of platinum and chlorine. Treating an aqueous solution of the sulfate with pure KOH, pure NaOH, an aqueous solution of ammonia, aluminum chloride, or barium chloride produced peculiar triple compounds. Elemental analysis of the compound indicated that it contained, by weight, 65.63% platinum, 8.06% oxygen, and 26.29% sulfuric acid (Davy, 1812c).

The last section of the paper described the preparation, composition, and properties of several triple salts of platinum obtained by the reaction of platinum sulfate with an aqueous solution of KOH, NaOH, ammonia, aluminum chloride, and barium chloride. It also described the preparation of fulminating platinum by the reaction of finely divided dry platinum sulfate with ammonia. The resulting compound was a light brown solid, lighter than fulminating gold, tasteless, insoluble in water, exploding violently when heated to 254.4 °C, and not exploding by percussion or friction. Fulminating ammonia was soluble in sulfuric acid and HCl, slightly soluble in phosphoric acid, insoluble in acetic acid, and decomposable by chlorine and gaseous HCl (Davy, 1812c).

In a following paper Davy reported that he had discovered a peculiar compound of platinum formed by the action of alcohol on platinum sulfate (Davy, 1820). He had put in vial equal volumes of a concentrated solution of alcohol sulfate and an aqueous solution of alcohol, and weeks later he had noticed that the dark color of the sulfate had disappeared, a dense black substance had precipitated while the remaining liquid phase had become colorless and transparent. Davy wrote that this liquid smelled like ether, had a strong acid taste, and produced a large amount of precipitate with barium nitrate. The dark substance could also be obtained by boiling a solution of platinum sulfate with alcohol (of any concentration) or ether (Davy, 1820).

Further examination showed that this substance, after being washed with water and dried, was tasteless, did not react with litmus paper, appeared in small lumps easily reducible to powder, and was not affected by cold or hot water or by air. Heated on a slip of platinum or paper, it exploded weakly accompanied by a flash of red light and leaving a residue of platinum. The substance was insoluble in sulfuric, nitric, and phosphoric acids, and slowly soluble in HCl. Added to an aqueous solution of ammonia it released very small air bubbles and after some time it became fulminating. In contact with ammonia gas the powder became red hot and scintillated; in contact with alcohol it decomposed completely producing acetic acid; mixed with sulfur flowers it produced platinum sulfide, and heated with phosphorus resulted in a brilliant combustion and formation of platinum phosphide (Davy, 1820).

Additional experiments showed that this particular substance appeared to be composed of almost pure platinum, accompanied by small amounts of oxygen and the elements of nitric acid. Davy believed that the small amount of impurities present was accidental and originated from the manner in which the platinum sulfate had been prepared.

Davy described several chemical reactions taking place with this substance. For example, contacting the powder with alcohol vapor at room temperature resulted in an immediate and highly exothermic reaction; the heat produced was enough for igniting the metal until the alcohol was exhausted and acetic acid formed. A variety of substances (i.e., sponge, cork, cotton, asbestos, etc.) generated heat and light when put in contact with the powder (Davy used this property to build a tinder box). Davy wrote: "it would be premature to speculate on the uses to which this powder may be applied, but from its peculiar properties there is reason to think it will admit of some useful applications" (Davy 1820). It would take Johann Wolfgang Döbereiner (1780-1849) and others to show how true this prediction was, and the importance of platinum black in catalytic reactions.

In the closing sections of this paper Davy described the effects of platinum sulfate on gelatin and its use as a test for gelatin, and the preparation and properties of a new gray platinum oxide (Davy, 1820).

Metal fulminates

Platinum

In an additional paper about fulminating platinum, Davy pointed out that gold and silver were known to react with ammonia to produce fulminating compounds. Gold and platinum seemed to be closely related metals having many common attributes: they were both soluble in the same solvents, they hardly combined with oxygen, chlorine, or sulfur, and their oxides formed peculiar complex salts with acid, alkaline, and earthy substances. These analogies suggested the possibility that platinum could also form, as gold, a fulminating compound. In this new paper Davy reported again that he succeeded in synthesizing this compound and found that its properties were similar to those of fulminating gold (Davy, 1817a).

Davy's procedure started by dissolving thin sheets of platinum in aqua regia, re-precipitating the metal with ammonium chloride, followed by reduction to the metallic state. The purified platinum was dissolved again in aqua regia, evaporated to dryness, the residue dissolved in water, precipitated with hydrogen sulfide, and converted into platinum sulfate by the action of nitric acid. The resulting solution was treated with a slight excess of ammonia and the resulting precipitate separated by filtration. This solid was partially dried, mixed with a solution concentrated solution of KOH, and then evaporated to near dryness by boiling. The mixture was filtered and the solid phase washed repeatedly with water and then left to dry at 100 °C. Davy described the resulting compound as a brown coherent powder, although the color varied according to the amount of alkali employed and the time of boiling the mixture. Very small amounts of fulminating platinum put on filtering paper and slowly heated to about 204 °C, exploded with a loud bang and tearing the paper. Davy wrote that the explosive force seemed to be exerted in all directions but principally downwards, and that a flash of light accompanied the explosion. All these characteristics were almost identical to those of fulminating gold. Davy found that both fulminates heated to 149 °C in contact with mercury, decomposed without explosion. Fulminant platinum exploded by friction but not by percussion (Davy, 1817a).

Davy added that platinum fulminate did not conduct electricity, was tasteless, insoluble in water and soluble in cold sulfuric acid and less soluble in hydrochloric and nitric acids. When heated in chlorine it decomposed releasing white fumes, ammonium chloride, and platinum chloride; it was also decomposed by hot ammonia and HCl gas. Heated with sulfur it decomposed quietly yielding platinum sulfide. Heated with common quicklime it gave an aqueous solution of ammonia and a little nitrogen. According to Davy all the above results indicated that platinum fulminate was a compound of platinum oxide and ammonia, more specifically, a triple compound of platinum oxide, ammonia, and water. Additional experiments showed that it contained, by weight, 73.75% platinum, 8.75% of oxygen, 9% of ammonia, and 8.50% water (Davy, 1817a).

The last section of the paper was devoted to some speculations about the formation and decomposition of platinum fulminate. According to Davy, when the triple compound of platinum oxide, sulfuric acid, and ammonia was boiled in KOH or NaOH, the sulfuric acid united with the fixed alkali, ammonia was partly expelled and the remainder combined with the oxide of platinum, generating fulminating platinum. Heating the latter in a closed vessel decomposed it

into nitrogen and ammonia gases, platinum, and water; the resulting explosion was the result of the sudden expansion of the gases generated (Davy, 1817a).

Silver

On May 23, 1831, Davy read a paper to the Royal Dublin Society (Davy, 1837b) where he mentioned that during his work on a new acid obtained by the action of nitric acid on different chlorides, he had observed the presence of some compounds, which spontaneously exploded when contacted with chlorine (Davy, 1831b). Further experiments of this phenomenon had led him to synthesize a new silver fulminate, different from the one discovered by Edward Charles Howard (1774-1816) in 1800 (Howard, 1800).

Davy prepared his new fulminate using Howard's mercury fulminant as the starting material. For this purpose he put a small amount (0.7 to 3.2 g) of Howard's material, dry or moist, into a phial containing about 14 g of pure and 0.13 g of zinc filings for every 0.7 g of Howard's material then closed the vial and let the mixture react under occasional mixing for 20 to 30 minutes. The liquid phase, containing the zinc fulminate, was then separated by filtration and treated with silver nitrate; the resulting white precipitate was the new silver fulminate. Davy remarked that this compound could be easily prepared by adding silver nitrate to a solution of any of the soluble fulminates. Davy wrote that the properties of the precipitate after being filtered, washed, and dried, either on the open air or at temperatures below 100 °C, seemed to be the same as Howard's silver fulminate. His fulminate, after dried in the filter, broke into small lumps, easily reducible to a white impalpable powder. On exposure to light the color changed from greyish white to yellowish brown, brick red, or even black. Davy warned that this material had to be handled with precaution because it exploded by percussion, by friction, by rubbing, or when heated to 177 °C. Other properties included being insoluble in cold water and sparingly soluble in hot water; it exploded instantly in contact with dry or moist chlorine and with concentrated sulfuric acid; HCl decomposed it into silver chloride and hydrogen cyanide, and dilute sulfuric into silver sulfate and fulminic acid. It was partially soluble in aqueous ammonia and in solutions of KOH and NaOH, forming crystallized fulminating compounds. According to Davy his new fulminating silver was composed of one part of silver oxide (118) and two of fulminic acid (84), that is, by weight, 58.42% silver oxide and 41.58% fulminic acid (Davy, 1837b).

Davy utilized the difference in the action of chlorine on silver bifulminate to develop a new very delicate test for detecting the presence of the element in a gas mixture. A very small amount of silver bifulminate (about 0.06 g) was enough to detect the presence of chlorine by the resulting instantaneous explosion. He illustrated his test by detecting chlorine in mixtures of chlorine with hydrogen, nitrogen, nitrous oxide, hydrogen cyanide, atmospheric air, CO₂, or HCl, vapors of diethyl ether, turpentine, naphtha, or acetic acid, in the gas released by the reaction of sulfuric acid and calcium chloride, of nitric acid and sodium chloride, etc. (Davy, 1837b).

Acetylene

In 1836 Davy reported that he had carried a series of experiments with the purpose of obtaining potassium in a large scale, in which he strongly heated in an iron vessel a mixture of calcined tartar (potassium hydrogen tartrate) and powdered carbon, in a ratio varying from 10:1 to 15:1 (Davy, 1836, 1837a). The remainder of one of these experiments was a dark gray soft granular mass, which adhered to iron tenaciously and decomposed readily when thrown into water, releasing a gas and leaving a carbonaceous residue. This gas was found to be was a mixture of hydrogen and a gas composed of carbon and hydrogen in nearly equal volumes. The latter burned in air with a flame

brighter than that of olefiant gas (ethylene), and deposited carbon when the combustion took place in the presence of a limited amount of air. It exploded spontaneously when brought in contact with chlorine, producing a red flame and depositing a large amount of carbon. Davy reported that this reaction took place in the dark or the presence of sunlight; the gas also exploded when mixed with oxygen, producing a mixture of water vapor and CO_2 . The complete combustion required 2.5 volumes of oxygen per volume of the gas. The brilliance of the flame suggested that it could be used for illumination purposes, if produced at a sufficiently low price (Davy, 1836, 1837a).

Further experiments with this gas indicated that it could be stored over mercury indefinitely, without change, at atmospheric pressure; water absorbed it slowly, up to a concentration of equal volumes. Upon boiling, the dissolved gas was released without chemical change. The gas was partially soluble in sulfuric acid producing a blackened solution. Analysis of the gas indicated that one volume of it contained one volume of hydrogen and two volumes of gaseous carbon (at that time hydrogen was considered to be monatomic), that is, the same amount of carbon and one half the amount of hydrogen present in olefiant gas. Hence, as said by Davy, it was a *bicarburet of hydrogen* represented by the formula $(\text{C}_2 + \text{H}_1)$ or $(2\text{C} + \text{H})$, a composition that indicates it was a completely new gas. The specific gravity and equivalent of the gas were 0.917 (air = 1) and 13.24, respectively (Davy, 1836, 1837a).

These carburets decomposed in water, forming the bicarburet of carbon, carbon, and potassium hydroxide (Davy, 1836, 1837a).

Davy's discovery remained a curiosity for about 20 years when Marcelin Berthelot (1827-1907) showed that the gas could be prepared by a variety of chemical reactions, for example, passing ethylene, ethanol vapor, ether, acetaldehyde, etc. through a red hot tube. Berthelot gave it the name *acetylene* and indicated that it was a *hydrogen quadricarbure*, which should be considered the type of the general series characterized by the formula $\text{C}_{2n}\text{H}_{2n-2}$ (Berthelot, 1860).

Milk adulteration

Davy wrote that potatoes and skimmed milk constituted a large portion of the daily food of the poor Irish classes and hence it was important that they should be supplied in the best form; for example, about 1,000 liter of skimmed milk was sold weekly in the markets of Cork. This fact led Davy to carry a series of experiments to determine a purity standard for skimmed milk and conclude that an instrument based on the principle of the hydrometer would be the simplest to carry on the job (Davy, 1821). In the first stage of this work he measured the specific gravity of a very large number of samples of genuine milk produced from local dairy farms, which he skimmed by himself, comprising all the varieties of cattle, soil, and modes of feeding, and also examined many specimens of *adulterated* skimmed milk from the markets. His results indicated that at 10 °C the specific gravity of a large number of genuine skimmed milk samples varied between 1.037 and 1.0375, with a maximum of 1.040 and a minimum of 1.036.

Davy wrote that since most people believed that skimmed milk was adulterated with water, chalk, flour, starch, sugar, etc., he had performed appropriate experiments to consider these possibilities. His results indicated that except for water, all the other additives were inappropriate: chalk was completely insoluble in skimmed milk and promptly precipitated; flour and starch increased the specific gravity of the milk but this effect was temporary because being insoluble they separated from the milk after a short period of time; the relative high price of sugar barred its use for the purpose, etc. Water was the obvious and most attractive additive; sometimes it was possible to add 20% of water to the genuine milk to reduce its density to that of skimmed milk. Distillation of the diluted fluid returned milk having the density of the genuine product. In Davy's words "skimmed

milk and water combine without undergoing any sensible alteration of volume, or condensation. Skimmed milk is of much greater specific gravity than water and its density is diminished in direct proportion to the quantity of water added to it" (Davy, 1821). Based on this fact Davy developed a lactometer, which differed little from the common hydrometer; the main difference was a scale adapted to the specific gravity of milk at 17.2 °C, the typical summer temperature at Cork. As described by Davy: "It is made of brass and consists of a pear-shaped bulb, at the top of which is a graduated stem and at the bottom a brass wire to the end of which a weight is screwed. The scale... is marked 0, which corresponds with the specific gravity of the lightest genuine skimmed milk, or 1.035, distilled water being 1.000. ...The dots and figures...indicate parts of water in 100 parts skimmed milk at 60°." According to Davy when the milk temperature was different from 60 °C the readings should increased (decreased) 1° for every 3 °F of temperature difference (Davy, 1821).

Detection of manganese

In 1850 Davy reported to the Irish Academy that he had developed a new and simple method for detecting the presence of manganese in inorganic and organic substances such as rocks, minerals, soils, and vegetable and animal substances. His method also allowed obtaining salts of manganese in a pure state (Davy, 1850b). In Davy's method the substance being examined was mixed with sulfur flowers and heated to red hot or less, in contact with air. The corresponding reaction converted the manganese to its sulfate and the sulfur to a mixture of its oxides. The presence of iron the raw material did not affect these results.

More details and examples were added in a following publication (Davy, 1850c). For example, heating a small amount of sulfur flowers with manganese over a slip of platinum foil to red-hot resulted in the formation of a mixture of manganese sesquioxide (Mn_2O_3), sulfide, and sulfate. Longer heating times increased the percentage of manganese sulfate in the final mixture. Washing with water and precipitation with potassium ferrocyanide easily separated the sulfate. Boiling in a closed vessel a solution of ferrous sulfate, manganese dioxide, and sulfur flowers, until the mixture produced a white precipitate with potassium ferrocyanide could also separate large quantities of the sulfate. The same procedure could be used for preparing manganese chloride using ferrous chloride instead of ferrous sulfate, or dissolving an excess of the dioxide in HCl. The sesquioxide itself could be prepared by heating to red-hot in an open vessel a mixture of manganese dioxide with peat mold, sawdust, or starch (Davy, 1850c).

Electrochemical analysis

In his first paper on the subject Davy wrote that he had used successfully the electrochemical principles described by Humphry Davy (Davy H., 1807) to build a simple apparatus able to detect small amounts of metals, particularly metallic poisons (Davy, 1831a). The experimental apparatus consisted of two metals, generally zinc and platinum, where zinc was positive and platinum negative with respect to all the other metals. These two poles were immersed in a mixture of few drops of an aqueous acid solution (HCl or sulfuric) and the metallic compound being investigated, forming an electrical circuit that deposited the metal on the negative surface. The zinc and platinum employed was commonly in the form of foil; sometimes, however, a small platinum crucible, or spatula was used. According to Davy, the size and thickness of the two poles did not affect the results, and the platinum spatula with the attached spoon was particularly useful when it was convenient to concentrate the sample by boiling to near dryness. For the purposes of the test it was enough to put on top of the platinum slip a mixture of a drop or two of acid with the compound being investigated, and then the liquid contacted with the zinc electrode (Davy, 1831a).

Davy went on to give a detailed description of the many experiments he performed to prove the effectiveness of his method for detecting the different combinations of the principal metallic poisons (i.e., arsenic, mercury, lead, and copper), and the precautions to be taken with each metal. Arsenic was particularly important because of its increased use for criminal purposes and the lack of a clear test for detecting its presence. Davy proved that his method was able to detect very minute quantities of the different metals, even when their compounds were mixed with a number of vegetable and animal substances. Thus, the existence of arsenic was readily detected when mixed with the ordinary foods such as wheat flour, bread, starch, potatoes, rice, peas, soup, sugar, gruel, tea, vinegar, milk, eggs, gelatin, wines, and also when mixed with the principal secretions of the alimentary canal. Arsenious acid was easily detected when mixed with butter, lard, oils, etc. Similar results were obtained when testing for corrosive sublimate, lead acetate, and copper sulfate, alone or in complex mixtures of organic substances (Davy, 1831a).

Davy remarked that the zinc he had used was shown to be free of arsenic, but not so the conducting acid. To test its presence he recommended putting one or two drops on a slip of platinum and contacting the two metals in the center of the drop. The appearance of a permanent bluish spot in the platina indicated that arsenic was present. This mark was smaller or larger according to the amount of arsenic present. The presence of arsenic in sulfuric acid was detected in a similar manner, except that that the acid was previously mixed with a small amount of HCl free of arsenic (Davy, 1831a).

In a following paper Davy described the experimental procedure for detecting the presence of arsenic(II) and arsenic(III) oxides, as follows (Davy, 1856-1857b): An amount of about 6.5 mg of the material being tested was mixed with a drop of ordinary concentrated HCl, then deposited on a slip of clean platinum foil and the liquid contacted with a slip of sheet zinc or foil. Any arsenic present was instantly reduced to metallic state on the surface of the platinum; the surface became iridescent and assumed a variety of colors. The affected area could only be cleaned with nitric acid or heating the foil with an alcohol lamp or candle. The heat caused the deposit to transform into arsenic(II) oxide while releasing its typical garlic odor. Davy found that the following compounds gave a positive result: potassium arsenate, calcium arsenate, arsenic(III) oxide, arsenic chloride, arsenic sulfide, etc. He also recommended that very dilute samples be first be concentrated by boiling to almost dryness. He also believed that his method was able to detect arsenic in the amount 1/2500 of a grain (0.065 g) and was not impaired by the presence of vegetable and animal substances, or by a mixture of both (Davy, 1856-1857b).

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