

The history of mercury. From discovery to incommmodity

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RESUMEN. El mercurio, a pesar de estar presente en muy pequeña cantidad en el mundo, ha representado un papel muy importante en el desarrollo de la alquimia, la extracción del oro y la plata, en la industria cloro-sosa cáustica, baterías, construcción de instrumentos científicos, tratamiento de enfermedades y control de plagas. La preocupación creciente acerca de la calidad del medio ambiente está llevando a una reducción importante en su producción anual y a su sustitución por otros compuestos.

ABSTRACT. Mercury is present in the world in very small amounts, but it has played a very important role in the development of alchemy, extraction of gold and silver, in the chloro-alkali industry, batteries, construction of scientific instruments, treatment of illnesses, and pest control. Increasing environmental concerns are leading to a significant reduction in annual production and to its substitution by alternative components.

DISCOVERY OF MERCURY

Archeological finds indicate that mercury has been in use for more than 2 500 years, but give no indication on how it was discovered. Arribas¹ offers a simple explanation, based on chapter Mercury of Primo Levi's (1919-1987) book *The Periodic Table*:² "One day, after a few periods of tremors, the prehistoric man that inhabited in an open cave in a mountainous system of volcanic origin, was surprised to observe that from the cracks in the ceiling, in addition to water, another strange shiny grey liquid oozed in thick drops that on hitting the floor burst into many small drops of high mobility. After collecting some of it he noted that contrary to other liquids the new one did not wet the hands but produced a cool feeling. He also observed that the new liquid was so dense that stones, pieces of lead or of iron floated on it, and that the liquid gave a silver color to the metals."

Mercury was much discussed by philosophers in the days of Aristotle (384-322 BCE) who record its use in religious ceremonies and called it fluid silver;³ Theophrastus (371-286 BCE) mentions the deposits of the Almadén region of Spain as an important source of vermilion for use in Greece and Rome and gives a general description of the purification of cinnabar for use as the pigment, and a method of preparing metallic mercury:⁴ "Spanish cinnabar, which is extremely hard and strong, is natural, and so too is that of Colchis... The manufactured variety comes from one place only, which is a little above Ephesus. Here, a sand which glows like scarlet kermes-berry is collected and thoroughly pounded to a very fine powder in stone vessels. It is then washed in

copper vessels, and the sediment is taken and pounded and washed again. There is a talent in doing this, for from an equal quantity of material some workers secure a great amount of cinnabar, and others little or none... The process is said to have been invented and introduced by Callias (one of the wealthiest men in Athens)... from the silver-mines, who collected and studied the sand, thinking that it contained gold owing to its glowing appearance. But when he found that it contained no gold, he still admired its fine color and so came to discover the process, which is by no means an old one, but dates back only some ninety years before the archonship of Praxibalus at Athens... Quicksilver... is made by pounding cinnabar with vinegar in a copper mortar with a copper pestle."

The extraction of mercury by roasting the ore and the property of amalgamation, have been described in detail by Roman writers. Vitruvius (90-20 BCE) wrote:⁵ "When the ore has been collected in the workshop, because of the large amount of moisture, it is put in the furnace to dry. The vapor, which is produced by the heat of the fire, when it condenses on the floor of the oven, is found to be quicksilver. When the ore is taken away, the drops which settle because of their minuteness cannot be gathered up, but are swept into a vessel of water; there they gather together and unite". He adds that four sextard (a sextarius was measure of volume equivalent to 0.547 L) of mercury weigh 100 librae and that a stone, however heavy, will float on mercury, whereas even a small piece of gold will sink, and concludes, "That the gravity of bodies depends on their species and not on their volume."⁶

In the first century CE, Pedanios Dioscorides (40-90 CE) of Anazarbus, Cilicia described the following process for preparing metallic mercury⁷: *“Putting an iron spoon having Cinnabaris in an earthen pot, they cover the Cup dawbing it about with clay, then they make a fire under with coals; and ye soot that sticks to ye pot, being scraped off & cooled, become Hydrargyrum. It is found also in ye place where Silver is melted, standing together by drops on ye roofs. And some say that Hydrargyrum is found by itself in ye mines. But it is kept in glassen, or leaden, or tinnen, or silver vessels, for it eats through all other matter, and makes it run out”*. Dioscorides distinguished between native and virgin quicksilver, called *argentum vivum*, and *hydrargyrum*, the name given to quicksilver prepared from cinnabar. The two were assumed to have different properties. He also pointed out that because of its red color cinnabar was sometimes confused with and at other times used as an adulterant for the red oxide of lead or minium. He prepared quicksilver from cinnabar by placing it in an iron vessel, which was then set in a clay dish; another clay dish was placed on the first as a cover, and all were luted together with clay. A charcoal fire was then placed under them and blown with a bellows. The top vessel collected a black soot that was washed for quicksilver.⁸

Pliny⁹ (23-79 CE) published the most ancient and complete description of cinnabar and vermilion: *“There is also a mineral found in these veins of silver which contains a humor, in round drops, that is always liquid, and is called quicksilver. It acts as a poison on everything and breaks vessel by penetrating them with malignant corruption. All substances float on its surface except gold, which is the only thing that it attracts to itself... to separate the quicksilver itself from the gold it is poured out on to hides... and exudes through them... and leaves the gold in a pure state... Minium or cinnabar is of great importance among pigments at the present day... The most famous mine being that of Almadén... as about 2 000 pounds per year are delivered to Rome... the price of selling it being fixed at 20 sesterces (equivalent to five denarius) a pound to prevent its going beyond limit... In the cinnabar mines of Almadén the vein of sand is pure, without silver... Persons polishing cinnabar in workshops tie on their faces loose masks of bladder skin to prevent their inhaling the dust... which is very pernicious. Cinnabar is also used in writing books, and it makes a brighter lettering for inscriptions on a wall, or on marble, even in tombs... Hydragirium or artificial quicksilver is made in two ways, by pounding red lead in vinegar with a copper pestle in a copper mortar, or it is put in an iron shell... in pans... covered with a... lid... and then a fire is lit under the pans.”*

Abu-MusaDschaafa-al-Sofi, or Geber (699 to 756), one of the most famous alchemists, assumed that quicksilver was the metallic essence of all metals, sulfur being the other component. Hence all metals were composed of varying proportions of sulfur and quicksilver. The sulfur content, being combustible, explained the change a metal experimented when heated, while the quicksilver content bestowed the metallic qualities, such as malleability and sheen. Although he did not recognize mercury as a metal, he regarded it as a substance of great consequence and is credited with having been the first to prepare red precipitate and to sublime mercuric dichloride in the course of his many experiments with it. He speaks of it as softening gold and was no doubt familiar with its properties of forming amalgams.⁸

Abu Bakr Muhammad bin Zakaria al-Razi, called Rahzes (850-923), Johanis Mesue (925-1015), and Ibn Sina or Avicenna (980-1037), used quicksilver, mercurial ointment, and mercury dichloride in treating itch and various other skin diseases; they also mentioned that the dichloride was poisonous. In due time, the use of quicksilver in medicine was definitely established by the Arabic physicians early in the Middle Ages of European history. Rahzes gave a fairly clear account of the synthesis of cinnabar. Part of his work, translated into Latin in the thirteenth century as *Raziz de Aluminibus et Salibus*, contains the following paragraph: *“There is another method, and it is the coagulation of mercury with the odour (vapor) of sulphur. That is, you put it in a piece of thick cloth, tie it, and suspend it in a vessel. Place sulphur in the bottom of the vessel and seal up the junction. Kindle a fire under it for the whole day, and then take it off the fire so that it may cool. There you will find a red salt uzifur (from the Arabic, zanjufur = cinnabar)”*.⁶

The ancient Egyptians knew and used tin and copper amalgams. Some mercury flasks have been found in tombs dating back to 1 500 or 1 600 BCE. From the sixth century BCE their literature makes increasing mention of mercury, its preparations and uses. The Leiden Papyrus, although it dates from the third century CE, contains compilations of much older materials, and includes some prescriptions that contain mercury.⁶

The ancient Chinese and Hindus also knew mercury. Its production seems to have started in China at about the same time as in the Mediterranean world, and apparently independently. Mercury and cinnabar are mentioned in the *Classical Pharmacopoeia* (Shen Nung Pem Tshao Ozing). Some time later in the first millennium CE Chinese alchemists prepared both corrosive sublimate and calomel by heating various mixtures containing mercury, salt, and alum, and made a clear distinction between them. The preparation of both chlorides is described in the *Great Pharmacopoeia* (Pên Tshao Kang Mu) compiled in 1596. A mercury still is known dating from the later Han dynasty (first or second century CE). The earliest mirrors also date from this dynasty; they consist of a polished layer of tin amalgam on a bronze plate.⁶ The Chinese alchemist Ko Hung (281-361 CE) wrote in the *Pao Yu Tzu*, *“Many do not even know that mercury comes out of cinnabar (tan sha). When told, they still refuse to believe it, saying that cinnabar is red, and how can it produce a white substance? They also say that cinnabar is a stone; that stones when heated turn to ashes: and how then can anything else be expected of tan sha?”* The mausoleum of Emperor Ch'i-Huang-Ti, who died in 210 BCE, contained a relief map of China in which the ocean was represented by a pool of quicksilver, and the Yangtze and the Yellow Rivers by flowing streams of quicksilver.⁸

As early as 500 BCE, India was using mercury as a drug. From there, its medical use was transmitted to Persia and perhaps to China. Up to about 1 000 CE mercurial drugs and alchemy as part of the gold making were not yet popular in Arthasastra. The use of mercury both in alchemy and medicine is found in India only in the later literature (earliest Tantric cult).¹⁰

The Arabs, after conquering the Iberian Peninsula, exploited the mines of Almadén and exported mercury and cinnabar. They used mercury as a decorative material, the most prominent example being the pool of mercury that was installed in the tenth century in the royal gardens at Medina Azahara (near the Alhambra).

The Italian deposits of Monte Amiata in Toscana were discovered early and were worked first by the Etruscans, then by the Greeks and still later by the Romans.

More detailed descriptions of the treatment of cinnabar and production of mercury began appearing around the sixteenth century in the first comprehensive metallurgical treatises, which were then being published. Those written by Vanoccio Biringuccio (1480-1538) and Georgius Agricola (1494-1555) are the best known.

Biringuccio in his *Pyrotechnia*¹¹ wrote: "*Since semi minerals are not produced by Nature as all rocks or all metal; they are called so by speculative physicians. Many kinds of these are found, those that resemble rocks are earthy, very difficult to liquefy, and much more adapted for adorning paintings than for anything else. Those that liquefy with fire, like sulphur, antimony... and others resemble the metals almost like brothers. Some others are more watery so that they dissolve in water... These are the salts, vitriol rock alum, and saltpeter. To these, as a watery thing, belongs also quicksilver, as it is commonly called because of its motion. Although it appears not only as a liquid, but very liquid, this is not all similar in its effects to any of the above... Quicksilver is a body that consists of flowing and liquid materials, almost like water with a shining whiteness; it is composed by Nature of a viscous, subtle substance with an overflowing abundance of moistness and coldness together. This composition in the opinion of the philosophic alchemists, is a thing that is very disposed to become metal, indeed they say that it is the original seed of all metals. When it lacks the warmth and dryness or the specific time that they require, it cannot congeal and so remains in the form that we see as an imperfect thing without becoming a metal... These clever investigators have also called it mercury in consideration of its properties, perhaps because of its resemblance to the planet of him whose actions place him between gods and men, according to the poets in their stories. Alchemists in the opinion cited above wish to prove at all costs that quicksilver is truly a defect of Nature so that they can hope to remedy it with their art... Among its other notable qualities it also has this, that it holds suspended as a light thing any metal that is placed on top of it in a vessel, and bearing it up, allows it to float. An exception is gold, which it embraces and instead of holding it in suspension, it draws it into itself to the very bottom... It is used for many things in medicine on account of its coldness. It is numbered among the poisons. It has the property of contracting the nerves of those workers which extract it from ore, if they are not very careful, and it makes the limbs of those who continually handle it weak and paralysed. Mixed with silver and then distilled it makes cinnabar, and likewise mixed with sal ammoniac it makes what is commonly called corrosive sublimate or hard silver*".

In book IX of his treatise, Agricola¹² wrote that the knowledge of mercury seems to have first appeared in Greek sources. Mercury was found in pools in mines and was cleansed with vinegar and salt and refined by being squeezed through the pores of canvas or soft leather. He described five different methods extracting mercury from its ore. One of them consisted in heating the raw material in single and double pots, another used a domed chamber in which green trees were added to dry wood to accelerate the condensation of the mercury, and a third involved an iron tripod and giant earthenware pots. Agricola realised that mercury vapors are heavier than air and for that reason they could therefore conveniently

be trapped in condensers beneath the reaction vessels. He also warned that if the fumes had a sweet odour it indicated that mercury was evaporating and that the workers had to move to the windward in order to avoid inhaling the fumes, which were dangerous and would cause loosening of the teeth.

In 1640 Alvaro Alonso Barba (1569? -1661), a Spanish priest in the mining area of Perú, wrote *El Arte de los Metales*¹³ mainly about the extraction of gold and silver. This book was important and kept secret in Spain, until the British Ambassador, Edward Montagu, Earl of Sandwich (1625-1672), managed to get a copy and translated it in 1669. Barba, referring to mercury, wrote: "*There was very little use or consumption of Quicksilver before the beginning of this new Silver age in the world, then they only wasted it in Mercury sublimate, Cinabrio, or Vermilion, and the powders made thereof called Precipitate, which are also called in Spain the powders of Juanes de Vigo, which have been used to such mischievous purposes that the world was said to have too much of them... it hath been used to collect the Silver together out of Oar, which is ground small... it is incredible how great a quantity is consumed by the Founders of Metals of this Kingdom: for if the abundance of Silver that hath gone out of this Kingdom bath filled the world with riches and admiration, by it may be estimated the consumption and loss of Quicksilver, which after a most extravagant expense thereof at first, being now by good experience regulated within terms of moderation, is found to be equal in weight to the Silver extracted; and very seldom that the waste is so little. . .*".

The name vermilion was given to cinnabar, much valued on account of its brilliant scarlet color, and largely used as a pigment or in the manufacture of red sealing wax.

Despite Barba's belief that mercury entered into the composition of all metals, he denounced as 'a great error' the widely held opinion "*that because for so many years the best Refiners in these Kingdoms have wasted at the least so much Quicksilver, as they have gotten Plate, therefore the Quicksilver is really and truly consumed in the operation*" Instead of the messy patio process (see below) Barba recommended that amalgamation be carried out in closed vessels with stirring, and that laboratory tests of the silver ores be used to determine the best additives.

The followers of Paracelsus (1493-1541) believed that all bodies were composed of the *tria prima*, salt, sulfur, and mercury, though these were not the substances ordinarily known by these names but symbols for qualities or principles. Robert Boyle (1627-1691) referred to the Paracelsian hypothesis in his book *Sceptical Chymist*,¹⁴ with these words: "*And certainly he that takes notice of the wonderful operations of quicksilver, whether it be common, or drawn from mineral bodies, can scarce be so inconsiderate as to think it of the very same nature with that immature and fugitive substance which in vegetables and animals chymists have been pleased to call, their mercury.*" Boyle, asserted that mercury was a "*mixt body*", which nevertheless retained its identity through many chemical changes: "*There are some mixt Bodies from which it has not been yet made appear, that any degree of Fire can separate either Salt or Sulphur or Mercury, much less all the three... How does this Hypothesis (of Paracelsus) shew us how much Salt, how much Sulphur and how much Mercury to make a Chick or a Pompion*".

To the alchemist, mercury symbolised the expectation of converting the base metals into silver, or gold, or

something even more valuable, which would possess its high density, mobility, sheen, freedom from tarnish, high surface tension, and the ease with which it wetted, dissolved, or amalgamated with other metals. Alchemists designed as mercurius every volatile substance, thus alcohol was mercurius vegetabilis and mercury mercurius communis. Later on, the name mercurius was used only when referring to mercury.¹⁵

According to Nicolas Lemery¹⁶ (1645-1715), who used to mock the alchemists, all alchemists employed basically the same approach to gold making, which involved the extraction and manipulation of an essential or spiritual part of gold, which they called (philosophical) mercury or the seed of gold. The alchemists attempted to extract this essence from the purest part of lesser metals through the action of fire or a spiritual liquor. Those who considered this essence to be a seed of gold claimed that it could grow a mass of gold just like the seed of a vegetable grows a plant. Lemery appended to his critique of alchemical gold making an examination of the alchemists search for the universal medicine or potable gold. He began by lecturing on the proper uses of gold in medicine: as a cure for "*frictious du mercure*", mercury poisoning. Since gold and mercury amalgamate easily, Lemery believed that one should ingest bits of gold to fix and interrupt the motion of mercury corpuscles that disrupted the normal functioning of the body.

In scientific work mercury began to acquire special importance after suitable glass apparatus was developed. In 1643, Evangelista Torricelli (1608-1647) showed that mercury in a sealed, inverted tube always sank to a level of about 76 cm. Afterwards, Blaise Pascal (1623-1662), Boyle, and others showed that the level was lower on a mountaintop. By 1662, Boyle showed that the mercury level was dependent on the outside air pressure, and thus that the weight of the column was equal to the weight of a similar column of air extending to the top of the earth's atmosphere. The first closed-glass liquid thermometers, made around 1654, consisted of a glass tube closed at one end and having a liquid reservoir of large dimensions filled with distilled colored wine as the thermometric fluid. The advantage of a liquid like wine was that its expansion was independent of air pressure. Mercury and water thermometers were also tried by the Florentines but abandoned because their expansion was too small. Later this problem was overcome by the simple artifact of making thermometers with finer bores, thereby increasing their sensitivity. By the middle of the 18th century mercury thermometers had superseded others because of their more uniform expansion. An important advantage of mercury was that unlike other thermometric fluids, it was available in a high state of purity.

The isolation of air and oxygen over mercury by Carl Wilhelm Scheele (1742-1786), Antoine-Laurent Lavoisier (1743-1794), and Joseph Priestley, (1733-1804) played an important part in elucidating the nature of air. Priestley initiated another important scientific use of quicksilver when he first used it to seal off water-soluble gases in making gas analyses.⁸

AMALGAMATION

The first indication of an amalgamation process being used on a large scale was given by the twelfth-century Moslem geographer al-Idrissi (1099-1166), who reported that mercury was an important article of trade in Egypt at that time, some being re-exported for the extraction of gold in the countries in the south. By contrast,

Biringuccio¹¹ treats amalgamation mainly as a method of recovering scraps of precious metals from the "*sweepings of mints, goldbeaters, and goldsmiths*". He still believed, as did the ancient authors (for example, Pliny) that "*having gathered this up (the amalgam) and passed through a deerskin purse or evaporated with an alembic, the silver or gold that is there remains in the purse at the bottom of the cucurbit*". Agricola, who copied much of Biringuccio's book, seems to have felt the amalgamation process for silver not worth mentioning; though he described the corresponding process for gold in some detail, and repeated the same mistake about the leather purse.⁶

Up to 1557 the consumption of quicksilver was relatively small, being used mostly for medicinal and cosmetic purposes. In that year, at Pachuca, México, Bartolomé de Medina developed the Patio process in which ore was mixed on a large stonework floor (a patio) with common salt and ferric iron salts, and reacted for several days. This oxidized the sulfide minerals and liberated silver as native silver or re-precipitated metallic silver from silver sulfides. It was then mixed with mercury, which amalgamated with the silver. The mercury was then separated from the ore and evaporated to recover silver. The new process increased the profitability of silver mining ten-fold and thus revolutionized the economy of New Spain, making silver miners very wealthy. One major disadvantage of this process was the requirement of large amounts of quicksilver. Alexander von Humboldt (1769-1859) estimates that Mexico used 40 to 45 t of quicksilver annually between 1562 to 1570 and 75 t annually between 1571 to 1585. The supply of quicksilver became the keystone of the tremendous silver-mining industry.⁸

The patio process has been described in more detail by Juan de Acosta:¹⁷ "*A mixture of ground and roasted silver ore with mercury and various additives (water, salt, vinegar, copper sulphate) was spread out on a paved area and mules, sometimes drawing rollers, were walked round and round on it.*" The amalgam was separated from the gangue by washing (there was much loss at this stage) and concentrated by squeezing through linen bags. Acosta knew, however, that the resulting near-solid product was not pure silver, but contained five parts of mercury to one of silver; and he described the distillation as follows: "*the silver remaining without changing the form, but in weight it is diminished five parts of that it was, and is spongy*". The 'loaves' of spongy silver were hammered into bars, and needed no further refining.⁶

MERCURY SOURCES AND PRODUCTION

Mercury metal is widely distributed in nature, usually in quite low concentrations. The terrestrial abundance is on the order of 50 ppb, except in mercuriferous belts and antropogenically contaminated areas. In soils, the average mercury content is about 100 ppb; in rocks it ranges from 10 to 20 000 ppb. Surface waters generally contain less than 0.1 ppb total mercury.¹⁸ The most important mineral of mercury is cinnabar, HgS, found in rocks near recent volcanic activity or hot spring areas and in mineral veins or fractures as impregnations; the metal is found native to a certain extent. In spite of its low vapor pressure, metallic mercury disperses rather quickly into the atmosphere and, with suitable air movements is taken up by plants and animals. Cinnabar ores are widely distributed, though it is probable that all the richest sources were exhausted long ago, since the ore-bearing veins are usually on the surface or at no great depth. It is believed that this ore was formed by the min-

eralization of alkaline sulfide solutions hence its occurrence in volcanic region. Natural air emissions from mechanical activity, wind erosion, and degassing constitute the largest proportion of emitted mercury.^{18,19}

As described by Goldsmith²⁰ mercury ore deposits occur in faulted and fractured rocks, such as limestone, calcareous shales, sandstones, serpentine, basalt, and others. Deposits are mostly epithermal in character, i.e., minerals are deposited by rising warm solutions at comparatively shallow depth. All known mercury ores are relatively low-grade ores, the average mercury content being about 1 % wt. On the average there appears to be more mercury present in the sediments of the upper lithosphere than in the magmatic rocks, which is believed to be due to the fact that large quantities of mercury has reached the surface of the earth by processes other than the weathering of igneous rocks. Such processes are the transport of mercury by magmatic and thermal waters; but the weathering of ore deposits of magmatic origin may have added materiality to the mercury now present in sedimentary rocks.²⁰

According to Goldsmith²⁰ all commercial deposits of mercury ores are connected with hydrothermal solutions related to magmatic rocks. The presence of bituminous substances has also been supposed to have influenced the formation of deposits of mercury ores, since they may act as reducing and possibly sulfurizing agents upon solutions of mercury compounds, for instance in the case of the deposits in bituminous limestones of Idrija in Slovenia and the deposits of Almadén in Spain. At magmatic temperatures the redox potential of the ferrous iron in magmas must in most cases be sufficient to transform mercuric compounds into mercury and thus force the metal into the gaseous exhalation products, where it can again combine with sulfur.²⁰

Spanish ores still contain up to (exceptionally) 7 % mercury, but in other parts of the world mercury contents of 0.3 per cent or even less have been profitably worked because of the simplicity of the extraction process. This is still basically the same as in ancient times; the cinnabar, concentrated if practicable by washing or flotation, is roasted in a current of air, with or without the addition of desulfurizing substances such as lime or iron oxide, using directly (called Bustamante furnaces) or indirectly heated furnaces. The condensate of crude mercury is then freed from soot, dust, and other impurities by a variety of appropriate methods including kneading and pressing the powder, simple wash with water, flotation, distillation and filtration. From medieval times until quite recently, by far the largest tonnage usage of mercury has been in the extraction of gold and (especially) silver by amalgamation.¹⁹

The Spanish deposits of Almadén have been mined for more than 2 000 years. The ore bearing deposits are porous sedimentary rocks that containing mercury sulphide (cinnabar). The richest strata contain 12 to 14 % mercury at a depth of 170 to 200 m. One ton of ore yields about one flask of mercury (34.473 kg).¹⁹ This mine has accounted for over 99 % of Spain's output and since 1920 has produced about 115 000 t. Almadén it is the oldest and most prolific mine in the world, as shown in the statistic table of Hylander and Meili.²¹

The Italian deposits are located at Mount Amiata in Tuscany and contain cinnabar and metacinnabarite, with about 0.2 to 0.8 % weight mercury. The third largest deposits in Europe are situated in Idrija, Slovenia, and contain cinnabar and native mercury. The ore contains about 0.5 % weight mercury. The Turkish deposits are located at Izmir-Ödemis-Haliköy, Konya-Ladik, and Konya-Sizma, those of Russia in Nikotovka in Ukraina, those of China in the provinces of Yunnan, Hainan, and Kweichow; those of the U.S. in California and Nevada, and the main Mexican ore deposits are located in Guerrero, Durango, Chihuahua, Guanajuato, San Luis de Potosí, Aguascalientes, and Querétaro.

In 1556 Bartolomé de Medina was sent to Mexico to apply his patio process of amalgamation. Mercury supplied for this purpose was produced in Spain, sold to Austria who shipped it to Mexico. During the seventeenth century the richest mine in the world was the Santa Bárbara at Huancavela in Perú. Production was started in 1566 and up to 1790 this mine had produced over a million and a quarter flasks. In the eighteenth century alone five hundred thousand odd flasks were mined, but the life of the mine was measured and output declined until in 1839 the mine was abandoned.²²

Hylander and Meili²¹ have recently published a very detailed analysis of the global production of mercury in the last five centuries, which includes a table of production per country and characteristic epoch. Some of the outstanding figures reported indicate that in this period, approximately one million tons of metallic mercury was extracted from cinnabar and other ores, half of it before 1925. Approximately half the mercury extracted has been used for mining of gold and silver. Roughly one half of the registered mercury has been extracted in Europe, with Spanish mines alone contributing one-third of the world's mined mercury. About one fourth has been mined in the Americas and most of the rest in Asia.

Table 1 shows mercury world production per country according to the U.S. Geological Survey.²³

Production estimates have a high degree of uncertainty because most countries do not report primary or byproduct production data because of environmental

Table 1. Mercury world production per country.²³

	1999	2000	2001	2002	2003
Algeria	240	216	321	307	300
China	200	200	190	435	610
Finland	40	76	71	70	65
Kyrgyzstan	300	257	300	300	300
Mexico	15	15	15	15	15
Morocco	10	10	10	9	9
Russia	50	50	50	50	50
Spain	433	500	500	300	150
Tajikistan	35	40	40	20	30
U.S.	NA	NA	NA	NA	NA
Total (rounded)	1 320	1 360	1 500	1 500	1 530

and health concerns. Mercury demand and production will continue to be affected by ongoing global environmental and human health concerns.

In the U.S. the last mine to produce mercury as its chief commodity was closed in 1992. The mine is now included in the list of Environment Protection Agency (EPA) Superfund Sites. Large percentages of mercury are today recycled in plant, as home scrap, to supply the chlorine-caustic industry, which is the largest domestic end use.

DEVELOPING THE KNOWLEDGE

Two important treatises of the eighteenth and nineteenth century are Macquer's *Dictionnaire de Chymie*²⁴ and Chaptal's book *Chimie Appliquée Aux Arts*,²⁵ which more or less summarize the knowledge about mercury up to the beginning of the nineteenth century. Macquer's description is very detailed, giving information about the properties of the metal as well as of its derivatives. Inspection of its contents reveals some amusing (by today's standards) concepts. For example, it says (a) "*although Lemery the younger (Louis Lemery, 1677-1743, the son of Nicolas) claims that mercury is completely insoluble in water; many good physicians are of the opinion that water which has been boiled upon mercury has the property of killing worms and other insects, from which they suspect that some mercurial parts are dissolved by water; (b) Mercury vapors can cause violent explosions, (c) By digestion in a strong heat, continued during several months, mercury undergoes a sensible alteration, it is changed into a reddish earthy powder, which floats on the surface of liquid mercury, this preparation is called mercurius precipitatus per se, (d) The exceeding fusibility of mercury and its great volatility, together with its great density and gravity, are properties, which appear contrary and incompatible. The density, gravity, and solidity of metals leave no doubt but that the earthy element enters in a great quantity into their composition... but on the other side, solidity and fixity seems to be essential properties of the earthy principle. How then shall we conceive that a substance composed almost entirely of the most fixed and refractory principle should be exceedingly volatile and perhaps the most fusible of all bodies? This undoubtedly proceeds from the presence of some other principle, which is eminently volatile and fusible. But what is this principle. Is it phlogiston or that principle that Becker has mentioned but not ascertained, and which he calls mercurial earth? (e) The acid of vinegar, and probably of other vegetable acids, seem to be capable of contracting a very intimate union with mercury, for the acetous mercurial salt is not only crystallisable but is also insoluble in water and, (f) Crude and fluid mercury taken internally produce no effect on the body, because the adhesion of its integrant parts to each other hinders their division and distribution or solution, without which it cannot have any effect. In its crude state, therefore, does nothing but load the stomach and intestines. It falls downwards but its weight and goes out of the body along with the feces...*"

RELEVANT ISSUES ABOUT MERCURY

(a) Physical aspects

Today mercury is described as a metallic element, which has the unique property of being liquid at ordinary temperatures, and not wetting glass or objects placed in it. Its atomic number is 80, atomic weight 200.6, with numerous isotopes 197 to 204; its specific gravity is about 13.6. The molecules are probably monatomic. It

is silvery white with a high metallic luster, which in thin layers transmits a bluish-violet light. The freezing point is $-38.89\text{ }^{\circ}\text{C}$. On freezing it contracts forming a white very ductile and malleable mass, easily cut with a knife, crystallizing in the isometric system, and having a specific gravity of 14.193 at the melting point. The metal expands very uniformly on heating and vaporizes at $357.3\text{ }^{\circ}\text{C}$. The vapor is colorless, with a specific heat of $0.1397\text{ J}/(\text{g}\cdot\text{K})$ and heat conductivity about two-thirds that of silver. Dry air, oxygen, carbon dioxide, nitrous oxide, ammonia, and most other gases at ordinary temperatures do not attack pure mercury, but humid air oxidizes it slowly. Sulfur and the halogens combine directly with the metal. The metal dissolves in solution containing chlorine and bromine. Mercury dissolves many metals forming amalgams. Mercury forms two sets of salts mercurous (as Hg_2O) and the mercuric (as HgO).

One of the few experimental works that Amedeo Avogadro (1776-1856) conducted in his scientific career concerned the determination of the vapor pressure of mercury at temperatures very close to its boiling point.²⁶ For this purpose he used an inverted glass siphon, connected to a flask, and immersed in a bath of olive oil that could be heated to the desired temperature. In addition to the measurements, Avogadro derived the following equation to compute the vapor pressure of mercury at very high temperatures (up to $300\text{ }^{\circ}\text{C}$, which was the upper limit of most mercury thermometers then used):

$$T = P \left(\frac{1-l}{L} \right) \quad (1)$$

where T was the mercury pressure when it reached the height L (mm) in the open branch, P the total pressure, and l (mm) the height that air alone would have reached at the same temperature and pressure, according to the ideal gas laws. Avogadro proceeded then to state his experimental results using an expression of the form

$$P = (1 + at)^m \quad (2)$$

where P was the vapor pressure in atmospheres and t the temperature relative to the boiling temperature of mercury, in units of $100\text{ }^{\circ}\text{C}$ [for example, in this scale the boiling temperature of water would be $(360 - 100)/100 = 2.6$]. Avogadro found for the range $230\text{ }^{\circ}\text{C}$ to $300\text{ }^{\circ}\text{C}$ $a = 0.4548$ and $m = 2.875$ and that eq. (2) predicted results very close to the experimental ones. He also found that at lower temperatures and lower pressures, where the experimental errors became very large, the fit was not good. Previous measurements by others such as Michael Faraday (1791-1867), had already determined that near $0\text{ }^{\circ}\text{C}$ the vapor pressure of mercury was almost zero. Avogadro considered that in order to describe the vapor pressure of mercury in the range 0 to $100\text{ }^{\circ}\text{C}$ it was necessary to employ an equation having more parameters, like the one proposed by Biot. Avogadro modified Biot's equation to the form

$$\log P = at + bt^2 + ct^3 \quad (3)$$

by considering that the vapor pressure of mercury at $0\text{ }^{\circ}\text{C}$ was one millimeter mercury. On the basis of the experimental measurements he determined the values $a = -0.64637$, $b = 0.075956$, and $c = 0.18452$. For temperatures below the boiling temperature of mercury the relative value of the temperature was to be taken as its

absolute value. Application of eq. (3) to a low temperature such as 0 °C (that is, $t = 360/100 = 3.6$), led to $P = 8.498 \cdot 10^{-8}$ mmHg, a result that did not agree with Faraday's findings that at 0 °C the vapor pressure was 0 mmHg (the actual value is 0.000 018 46 mmHg). Avogadro attributed the numerical difference to physical reasons not related to the law that described the vapor pressure.

On 1817, the *Académie des Sciences* announced the annual competition for the prize in physics.²⁷ The stated topic was in three parts: (a) to determine the movement of the mercury thermometer as compared to that of an air thermometer from -20 to 200 °C; (b) to determine the laws of cooling in a vacuum; (c) to determine the laws of cooling in air, in hydrogen and in carbonic acid (today CO₂), at different degrees of temperature and for different states of rarefaction.

The competition announcement stimulated Pierre-Louis Dulong (1785-1838) and Alexis-Thérèse Petit (1791-1820) to continue the work they had previously done on the subject, and resulted in three fascinating publications, notable for the originality of the approach, hence theoretical and hence experimental.²⁸⁻³⁰

In their first publication²⁸ Dulong and Petit approached the problem of measuring the coefficient of expansion of mercury by a very ingenious procedure, based on the principle of communicating vessels. Two vertical columns of mercury, one hot and one cold were connected by a thin horizontal tube of negligible volume. At the equilibrium the columns were balanced, the pressures were identical, and thus

$$h_1 : d_1 = h_2 : d_2 \quad (4)$$

were h and d were the height and density in the respective column. The height could be measured easily and very precisely with the help of a cathetometer. Since density is inversely proportional to the volume, a simple and accurate method was now available for measuring the expansion of mercury, without reference to the material and shape of the vessel. The only care to be taken was that the bore of the tube should be constant and sufficiently large to make the capillary effect negligible.

Numerical calculations by this method indicated that the expansion of mercury increased from 0 at 0 °C to 1/5 300 at 300 °C.

Construction of a "weight" thermometer is probably one of the most interesting parts of this work and it was also used by Dulong and Petit to determine the expansion of other solids (Pt, Fe, Cu, and glass). It was helpful for determining the dilation of the principal substances and for a rigorous comparison of the different thermometers employed then. Dulong and Petit came in favor of the air thermometer as the ultimate standard, convinced that increments of temperature indicated in this instrument, or indeed on any gas thermometer, were increments in the true temperature.

About thirty years later Dulong and Petit's measurements were improved substantially by Victor Regnault³¹ (1810-1878). In addition, Regnault measured the compressibility of mercury.³²

Until the middle of the eighteenth century, chemists believed that fluidity was an essential property of mercury. On December 26th, 1759, Joseph Adam Braun, Professor of Philosophy at the University of St. Petersburg, using a mixture of snow and nitric acid, observed that a mercury thermometer sank to very low temperatures, which in one instance he recorded as -556 °F (!). On removing the thermometer he found the mercury

to be completely solidified. His measurement of the temperature was, however, completely erroneous, because he was unaware that mercury, unlike water, contracts during solidification, and imagined that the descent of the mercury in the stem of the thermometer took place while the mercury was still in the liquid state. The experiment was also vitiated by such circumstances as adhesion of the mercury to the walls of the stem and hollows left in the bulb as the metal assumed the solid state.

Braun's results attracted great interest in the scientific community and one of the results was the request by the Royal Society to make experiments on mercury freezing at Albany Fort in Hudson's Bay. These were performed in the winter of 1777-1778 by Thomas Hutchinson, Governor of Albany Fort, using freezing mixtures of nitric acid and snow, and an alcohol thermometer to check the readings of his mercury thermometers. During the first two winters the thermometer froze several times, with the fictitious recording of the supposed degree of cold, which had been attained. The alcohol thermometer, however, never recorded a temperature below -46 °F. It was thus clear that mercury could be frozen, as Braune had observed, but at a temperature closer to that recorded by the alcohol thermometer. This research was followed by another made by Henry Cavendish (1731-1810), in which it was found that the true freezing temperature of mercury must be between 39 to 40 °F below zero.³³

(b) Chemical aspects

Chemists of India prepared the mono- and dichlorides of mercury as early as the twelfth century. A detailed description of the process was given in the thirteenth or fourteenth century, and involved heating a mixture of common salt, brick dust, alum, Indian aloe, and mercury for three days in a closed earthen pot. The Japanese and Chinese also prepared calomel by similar methods.

A method for preparing a rather pure mercurous chloride (calomel) was known to the French physicians before 1608 (78). Jean Béguin (1550-1620) in his "*Tyrocinium Chymicum*", published in 1608, described the process: Corrosive sublimate was rubbed with as much mercury as could be "killed" or made to combine with it.³⁴

In 1788, three years after Claude-Louis Berthollet (1748-1822) had shown ammonia to be a compound of nitrogen and hydrogen, Antoine-François Fourcroy (1750-1809) started studying the action of ammonia upon different salts of mercury. For example, he found that the sulfate and nitrate of mercury were precipitated by ammonia as a grey or black oxide, with evolution of nitrogen. His work led him to believe that there were three distinct sulfates of mercury, in which the mercury combined with varying amounts of oxygen and sulfuric acid.³⁵ In 1801, in collaboration with Louis-Jacques Thénard (1777-1857), he made a masterly study of the oxides and some salt of mercury and definitely established the existence of two series of compounds, containing mercury in different degrees of oxidation³⁶ (it was stated that this research was completed 5 years before). During their study of the reaction between mercury, nitric acid, and alcohol, Fourcroy and Thénard found that a fulminant compound was formed after several minutes, but that after thirty minutes the product was a yellow powder, which did not detonate and contained no nitrogen; this they considered to be oxalate of mercury. Edward Charles Howard³⁷ (1774-1816) had pre-

viously (1799) obtained the fulminant compound mentioned above, but Fourcroy and Thenard found that another compound, which detonated when dropped in hot charcoal, was obtained as an insoluble powder when red oxide of mercury was digested several days with ammonia. This fulminant ammoniacal oxide of mercury was probably Millon's base ($2\text{HgO} \cdot \text{NH}_3 \cdot \text{H}_2\text{O}$) (see below) for it was found to form salts with sulfuric, nitric, and hydrochloric acid.

Fourcroy and Thenard also described the preparation and properties of the two nitrites of mercury, which had not been previously reported. The nitrite of slightly oxidized mercury, which was easily crystallized, was the initial product of the action of cold nitric acid on mercury; the nitrite of highly oxidized mercury was a deliquescent substance, formed in the early stages of the reaction between hot nitric acid and mercury.

Treatment of a solution of mercury in nitric acid with sal ammoniac and salt of tartar (that is, ammonium chloride and potassium carbonate) gave, under some conditions, a fusible white precipitate, $\text{HgCl}_2 \cdot 2\text{NH}_3$. By varying the conditions of preparation, an infusible white precipitate could be obtained, first noted as being different from the other by Lemery in 1663. This substance still appears in modern Pharmacopoeias as *mercurius praecipitatus albus*. Its composition was later found to be NH_2HgCl .⁶

In 1808 Thomas Johann Seebeck³⁸ (1770-1831) found that if a pool of mercury were placed on a block of ammonium carbonate and an electric current passed with the mercury as cathode, the metal would froth up to a buttery mass, which slowly decomposed, giving ammonia and hydrogen. This discovery aroused tremendous interest and the new 'amalgam' was studied by many other chemists, including Jöns Jacob Berzelius (1779-1848) and Humphry Davy (1778-1819).⁶ The existence of an ammonium amalgam enabled André-Marie Ampère (1775-1831) to propose a solution to this problem, with ammonium (NH_4) as what became known later as a "compound radical":³⁹ "*On ferait disparaître cette difficulté en admettant que, de même que le cyanogène, quoique ce soit un corps composé, présente toutes les propriétés des corps simples susceptibles d'acidifier l'hydrogène, la combinaison d'un volume d'azote et de quatre volumes d'hydrogène, qui est unie au mercure dans l'amalgame découvert par M. Seebeck, et au chlore dans l'hydrochlorate d'ammoniaque se comporte comme les substances simples métalliques...*" (This difficulty [the great similarity between ammonium salts and those of sodium and potassium] would disappear if we suppose that like cyanogen, which although a compound body, has all the properties of the elements which combine with hydrogen to form acids, the compound of one volume of nitrogen with four volumes of hydrogen which combines with mercury in the amalgam discovered by M. Seebeck, and with chlorine in ammonium chloride, behaves in all the compounds which it forms like the metallic elements...)³⁹

In 1846, Eugène Auguste Nicolas Millon⁴⁰ (1812-1867) discovered an additional important compound between nitrogen and mercury, in the reaction of yellow mercuric oxide with aqueous ammonia. It was basic (Millon's base) and formed a series of salts; its composition can be written as $(\text{HgOH})_2\text{NH}_2\text{OH}$.⁶

The discovery of oxygen by Priestley resulted from the fact that heating mercury at low temperature in the presence of air leads to the formation of the red mercuric

oxide. The oxide decomposes into mercury and oxygen when heated at higher temperatures.

Organometallic chemistry started in 1849 when Edward Frankland, discovered that metallic zinc would react with methyl iodide.⁴¹ Two years later he extended this reaction to other metals.⁴² Shortly thereafter, Nikolay Zinin (1812-1880) found that the more reactive allyl iodide readily formed $\text{C}_3\text{H}_5\text{HgI}$ even without the assistance of sunlight.

George Bowdler Buckton (1818-1905) discovered the mercury dialkyls in 1858, while trying to make methylmercuric cyanide by double decomposition, but the reaction took an unexpected course and he isolated mercury dimethyl as a heavy volatile liquid.⁴³ Interest in mercury organic derivatives became strong again when Otto Dimroth (1871-1940) discovered the mercuriation reaction, in which the reaction of mercuric acetate and benzene yielded phenyl mercuric acetate.⁴⁴ The reaction occurred much easily when using substituted benzenes, such as phenols, phenol ethers, and derivatives of aniline.⁶

PHARMACEUTICAL AND MEDICAL ASPECTS

According to Farrar⁶ as early as the ninth century Arabic physicians were making ointments by dispersing mercury in a vehicle such as animal fat, which prevented the droplets from recombining. These ointments were prescribed for skin and eye infections and became known in Europe, partly through the Crusaders who brought back knowledge of unguentum sarracenum and partly through the writings of Avicenna.

In 1180, Ruggiero Frugardi of Palermo recommended mercurial salves for chronic dermal and parasitic infections and by the sixteenth century mercury began to be widely prescribed in Europe, in spite of the accumulating evidence about the dangers of mercury vapor. Mercury poisoning in mercury mines was described among others, by Gabriele Fallopius (1523-1562) in his *De Metallis et Fossilibus*, by Pietro Andrea Mattioli of Siena (1500-1577) and Pieter van Foreest of Delft (1522-1597). In 1556, Agricola, when discussing the distillation of crude mercury just remarked:¹² "*The pots, lest they become defective, are moulded from the best potters' clay, for if there are defects the quicksilver flies out in the fumes. If the fumes give out a very sweet odour it indicates the quicksilver is being lost, and since this loosens the teeth, the smelters and others standing by, warned of the evil, turn their backs to the wind, which drives the fumes in the opposite direction; for this reason, the building should be open around the front and the sides, and exposed to the wind*".⁶

In 1665 probably the first standard for occupational health was introduced in the mercury mines at Idrija, where the workday was reduced from 14 to 6 h. At the turn of the century, Bernardino Ramazzini, (1633-1714), considered the father of occupational medicine, published his *De Morbis Artificum* (1713), in which he pointed out mercury and other metals as an occupational hazard in miners, gilders, chemists, potters, tin-smiths, glass workers, mirror makers, painters, and medical personnel.⁴⁵

Lemery gave the following explanation for the effects of mercury vapor:¹⁶ "*Those who draw it out of Mines, or work much with it, do often fall into the Palsie, by Reason of Sulphurs that continually steam from it; for these Sulphurs consisting of gross Parts, do enter through the Pores of the Body, and fixing themselves rather in the Nerves, by Reason of their Coldness, than in the other*

*Vessels, do stop up the Passage of the Spirits, and hinder their Course.*⁶

In 1719, Bernard de Jussieu visited the Almadén mines (Spain) and wrote a paper⁴⁶ describing the process of mercury extraction as well as the working conditions. He was surprised to find that the fumes did not injure the crops, trees, and inhabitants, and that springs near the mine yielded good potable water. The slaves who worked and ate in the mine however suffered severely from mercury poisoning. Although he mentioned tremor, which was due, according to him, to the *"tristes effets du sejour du sang dans des vaisseaux du cerveau devenus variqueux par le poids de quelques particules mercurielles"* (the sad effects of the residence of blood in the vessels of the brain, which have become varicose due to the weight of several particles of mercury) he attributed this ailment mainly to the workers carelessness or negligence in work. For him, *"la malignité arsenicale prétendue du Mercure"* (the pretended arsenical malignity of mercury) was ascribable more to myth and prejudice than to reality.⁴⁷

Paracelsus classified mercury as one of the three natural elements of blood, but he was aware of its possible toxic effects. According to him, mercury is at the origin of illness when it becomes *"agitated"* in the body by external heat. Three reactions are possible: distillation, sublimation, or precipitation, and from these processes evolve different symptoms. Paracelsus dedicated a whole monograph to miners' diseases due to mercury. In this book,⁴⁸ he described several symptoms of intoxication, such as tremor (*"shivering without feeling cold"*), gastrointestinal disturbances, oral infections, and blackening of teeth, and a two-phase treatment for mercury poisoning. In the first stage the patient was immersed in a hot herbal bath, the heat made the mercury mobile so that it could be excrete in the second phase. The patient was then covered with corrosive plaster that generated openings through which the metal flowed out. Paracelsus his responsible for introducing mercury in the pharmacopoeia in Europe and in the treatment of syphilis (see below).⁴⁷

Lemery, in his *Cours de chimie*,¹⁶ used his theory about the structure of salts to explain the toxicity and corrosive action on tissue of mercuric chloride: *"The Corrosion of Sublimate does proceed from the edged Acids which fix in the body of Mercury, and it may be said with great Probability, that this Metal always retaining a round Figure (let it be divided never so subtilly) does rarifie by the Heat of Fire into an abundance of little Balls, which the acid Spirits do fix into on all Sides, and so interlace themselves in it, that they hinder its rising higher, and do together make one Body, that is called Sublimate. But when this Sublimate is applied to Flesh, the Heat and Moisture of it do set in Motion the Mercurial Parts, and the Motion of the little Balls being once raised, they rowl about with great Fury, and tear the Flesh with the Edges they contain, which are like so many little Knives cutting wherever they touch; from whence it comes to pass, that if the Sublimate should be taken inwardly, it kills in a very little Time..."*

Use of mercury became common practice in the early years of the sixteenth century in the therapy of syphilis. The body of the patient was smeared completely with a mercury unguent for a period of weeks or months; a treatment that was accompanied by many bad side effects such as salivation, loose teeth, swollen gums, and bladder irritation. The discovery of calomel (Hg_2Cl_2), which is sparingly soluble, relatively non-toxic, and a

powerful purgative, was regarded as a great step forward. The name of calomel was given to it by Theodore Turquet de Mayerne (1573-1655), physician to James I of England another royal sufferer from syphilis. Lemery¹⁶ believed that the cure was through ingestion of large amounts of mercury: *"Mercury is given in two or three Pounds, and is voided again by Siege to the same Weight; it is better to take a great Deal of it than a little, because a small Quantity might be apt to stop in the Circumvolutions of the Guts, and if some acid Humours should happen to join with it, a Sublimate Corrosive would be there made; but when a large Quantity of it is taken, there's no need of fearing this Accident, because it passes quickly through by its own Weight."*

Many complex organic mercurials were made in the hope of reducing toxicity, and usually rejected after a short trial. A more rational approach to the use of mercurials in medicine began with Robert Koch's (1843-1910, 1905 Nobel Prize in Physiology or Medicine) claim that mercuric chloride was a more effective bactericide than the carbolic acid (phenol) popularized by Joseph Lister (1827-1912). Koch's claims led to the investigation of the bactericidal effects of more complex mercury compounds, such as the mercury salts of organic acids, which resulted in the manufacture of the well-known bactericides Afridol, Mercurochrome, and Merthiolate.⁶ The first really hopeful alternative to mercury came with the introduction of Salvarsan (arsphenamine) by Paul Ehrlich (1854-1915; 1908 Nobel Prize in Physiology or Medicine) in 1911.

ENVIRONMENTAL PROBLEMS

The toxicity of mercury and its compounds depends predominantly on their solubility, which determines absorption and distribution in the organism. Thus metallic mercury and all mercury compounds are toxic, with the exception of red mercury sulphide, which is practically insoluble in the body. Mercury causes acute damage to the lungs and chronic damage to the central nervous system. Mercury salts are caustic to the mucous membranes of the gastrointestinal tract and nephrotoxic when absorbed. Salts of bivalent mercury are more toxic than the monovalent ones, regardless of the route of administration. Since most organic mercury compounds are lipid soluble the solubility may lead to toxic dermatitis and severe damage the central nervous system. Mercury is mutagenic, teratogenic, and embryotoxic, especially in the form of alkyl compounds.¹⁹

As shown by the data Hylander and Meili,²¹ there has been a substantial increase in the background concentration of mercury during the last few centuries. Since the beginning of mercury mining, millions of tons of the element have been taken from beneath the earth where it was combined and liberated finally into the air or the sea. Mercury is a globally spread pollutant due to its low melting and boiling points, conversions between chemical forms, and participation in biological cycles. As a result of anthropogenic emissions, the global atmospheric deposition rate of mercury is approximately three times higher than in pre-industrial times. The main sources of human activity that lead to mercury release are chlorine-caustic soda production, coal-fire power plants and industrial boilers, hazardous waste disposal, municipal and medical waste disposal, and recycling. Volcanic activity, artisan gold mining, and mercury mining are other sources of mercury releases on a global scale. Much effort has been invested in reducing mercury emissions from the above anthropogenic sources.

Unlike lead, mercury is fairly rapidly eliminated by the body, and is not a cumulative poison; but, unlike arsenic, there is no evidence of acquired tolerance to continued small doses.⁶

Since the beginning of the nineteenth century there has been a steady increase of experimentation with mercury and its derivatives and also the reporting of severe intoxications of diverse origins, which in several cases, has taken serious dimensions.

Organomercury compounds in the environment constitute a much more serious threat than direct release of the metal. Compounds of the heavy metals have been known and used for long, as powerful fungicides known. From about 1950 onwards, phenyl mercuric acetate and related compounds were used in enormous quantities to control 'slime', (a viscous microbial growth) in paper mills. The effluent from these mills, discharged into rivers, lakes, or enclosed seas such as the Baltic, gave rise to concentrations of mercury in mud and water that caused justifiable concern. No definite ill effects were ever traced to this practice, but environmental considerations led to their replacement by non-mercurial germicides.⁶ The most famous case is probably the Minamata disaster, which attacked a poor fishing community on the island of Kyushu, Japan. The first cases were noted in 1953, and three years later the epidemic had reached such proportions as to demand a full investigation. Eventually it was found that the poisoning was caused by the effluent waters from the Chisso factory, which manufactured acetaldehyde using a catalyst based on methyl mercury. Fish and seafood became contaminated and especially affected fishermen and their families.⁴⁷

These accidents and many others have led to the increase awareness about the toxicity of mercury and to implementation of severe national and international legislation limiting the use and the amounts of mercury that can be discharged into the environment. For example, the EPA has set a limit of 2 ppb mercury in drinking water; the U.S. Food and Drug Administration, a maximum of 1 ppm of methyl mercury in seafood; and the U.S. Occupational Safety and Health Administration a limit of 0.05 mg of metallic mercury vapor per meter cubic in workplace for an 8-hour shift and 40-hour work week.

All these measures have led to a substantial decrease in the amount of mercury being used industrially. In 2003 world mercury production was estimated to be 1 530 t/year, which was less than the 2 200 t/year average world production from 1990 to 2000. This decrease has been achieved by recycling the metal and by development of alternative manufacturing methods or using less harmful elements.

For many years the principal use of mercury has been as a cathode in the electrolytic production of chlorine and caustic soda from brine. Sodium is removed from the sodium-mercury amalgam, and the mercury recycled within the chlorine-caustic soda plant as home or in-plant scrap. In the U.S., this industry accounts for 50 % of the domestic mercury consumption. An interesting comparison is that 60 % of the chlorine and alkali production in Europe is done with mercury cells, while the corresponding figure in the U.S. is 13 %. Diaphragm and membrane cells are alternative methods for chlorine-caustic soda production and do not use mercury.²³

Mercury in varying amounts is used in automobile convenience switches, barometers, computers, dental amalgam, manometers, mercury-vapor and fluorescent

lamps, thermometers, and thermostats, cleansers, pesticides, folk medicine, and skin lighteners. For most of these uses alternatives have already been developed: Lithium nickel-cadmium, and zinc-air batteries are substitutes for mercury-zinc batteries, indium compounds substitute for mercury in alkaline batteries, dental amalgams can be replaced by ceramic composites, and mercury in thermometers and other measuring devices can be replaced by ethanol and other liquids or by digital thermometry. Organic compounds have replaced mercury fungicides in latex paint, and digital instruments have replaced mercury instruments in many applications.²³

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