

Mercury and Mercury Electrodes: The Ultimate Battle for the Naked Existence (A Consideration)

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- Dedicated to the memory of Prof. RNDr. PhMr. **Robert Kalvoda**, DrSc. •

Abstract: In this article, the current status and position of mercury as one of the most typical representative of present day's fear from "harmful chemistry" is for the first time concisely reviewed (with 100 refs.). Mercury as such means a danger for the environment and the human beings, but the contemporary life of the civilized man without utilization of this metal element would be hardly imaginable. It is shown that mercury has occupied a significant position in the industry (in mining, as an inevitable component of electrolyzers, batteries, and various lightning devices), in medicine (as amalgams in dentistry or some special medicaments), as well as in physical and chemical laboratories (thermometer and barometers, or as traditional electrodes for polarography and voltammetry). Such a usage of mercury is considered in relation with toxicological aspects, from almost harmless liquid mercury, *via* potentially harmful Hg₂^{II}- and Hg^{II}-precipitates, up to highly poisonous Hg-vapors or deadly toxic organomercury compounds. The individual forms and compounds are characterized, also using less known or even extreme examples from the past, recent time, as well as from the present, including rather curious reflections of the so-called mercuriophobia. Regarding the evaluation of the actual toxicity, numerous inquiries concerning exposures to mercury have been extracted from the *Czech Toxicological Information Center (CTIC)*, gathering the respective data over the period of 1995-2011. Finally, some future prospects — mainly, in context with nowadays hugely popularized "green chemistry" — are given and possible consequences outlined.

Keywords: Mercury; Elemental form; Mercury compounds; Industrial and laboratory use; Toxicological profile; Electrochemistry and mercury electrodes; Present and future; Review.

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Introduction

As generally known, mercury is present in our environment as the only liquid metal element under common temperature (see Fig.1). For some people, this metal represents a high danger in any form and dose. Nevertheless, the specialists — and, in fact, almost everyone who wants to be informed — are aware of the fact that this danger is often being dramatized.



Fig. 1: Due to a high surface tension, liquid mercury readily forms compact droplets; regardless if the resultant aggregates are large drops at a wooden desk (left) or tiny droplets in the nanometer scale as the film deposited onto a carbon paste surface (right) [Illustrative photos from authors' archives]

Retrospectively, the human life has been accompanied with mercury for many hundreds or even thousands of years, when the anthropogenic sources of mercury cover *ca.* 60% of its present amount in the nature. In other words, up to about 40 % of the total quantity of this metal in the man's neighborhood occurs almost independently of human activities *via* soil erosion, volcanic activity, wood fires, evaporation of oceans, *etc.* (see *e.g.* ref. [1]). Regarding the former, *i.e.* the anthropogenic activities, there are many branches through which the unique metal element comes into environment [2]. Herein, one can mention the most important areas:

- Mining industry (*e.g.*, extraction of gold by amalgamation; see also Fig. 2)
- Industrial electrolysis
- Batteries and accumulators
- Lightning devices (discharge and fluorescent lamps, saving light bulbs; see Fig. 3)
- Measuring devices (thermometers, Fig 3; barometers, electrochemical analyzers);
- Paints and painting additives;
- Dentistry (silver amalgams);
- Drugs (historically *e.g.* calomel, Hg_2Cl_2 , recently controversial *Merbromin*, an organo-mercury halide).



Fig. 2:

Mercury (or Quicksilver) fountain in Barcelona installed in memory of the miners who had worked hard and many died in famous mercury mines.*

[Illustrative photo withdrawn from the authors' archives]

***Note:** The monument honors the mercury mines in Almadén, a Spanish town in the province of Ciudad Real, situated approximately 200 km south of Madrid. The town is known worldwide for mercury mining. Globally, the reservoirs of liquid mercury in this locality represents the largest quantity of the metal deposited and exploited at one site. It can be estimated that *ca.* 250,000 metric tons of mercury have been produced there in the past 2,000 years. Since 2000, the mines are closed and preserved as a museum complex.

Of course, the mass production and utilization of any element or of its compounds must be considered from every aspect, in the case of mercury predominantly the toxicological point of view. It is without doubt that the chemistry of this liquid metal includes many highly harmful substances; nevertheless, the recent and the present aversion against mercury are often inadequate and the fear exaggerated. Momentarily, we are witnessing the culmination of these anxieties from mercury, resulting in a true **mercurophobia** – a spontaneous movement of wide communities, comprising: (i) general public, often self-represented by various reporters; (ii) various eco-activists, usually well organized; and (iii) some environmentally (too) oriented scientists; all having the same goal – to remove mercury and its compounds from the industry, laboratories, and from ordinary life. And needless to say that such efforts can also be successful, as documented on some contemporary acts (see *e.g.* the respective resolutions of the European parliament [3] or already imposed total ban of mercury in Scandinavia [4]).

Strict ecological and safety rules being introduced to the public life (*via* the concept of the so-called "**green chemistry**"), as well as various popular prejudices, fears and faults, are naturally reflected in the present day's unfavorable situation about practical use of mercury in industry and medicine, or in physicochemical laboratories.

Concerning the lastly named, for a nearly century, the electrochemists and electroanalysts almost could not envisage their research work without the liquid mercury-based working and auxiliary electrodes, as well as calomel-containing reference electrodes.



Fig. 3: Occurrence of mercury in common life. From above: discharge lamp; below, on left: the tip of thermometer (with Hg filling); right: skin tanner (with low-pressure Hg-vapor lamp and a pair of infrared heaters).

(Illustrative photos taken from free access website [2])

Starting in the early 1920s, with the discovery of *dropping mercury electrode* (DME) for polarography [5] (see Fig. 4 and ref. [6]), continuing through the 1930s, 1940s, and 1950s that had spawned the ultimate solution for the proper construction of the *hanging mercury drop electrode* (HMDE [7]; Fig. 4), up to the recent decades, where both DME and HMDE could be finely combined with modern instrumentation [8].

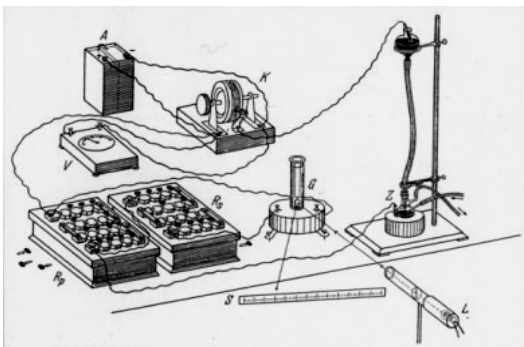


Fig. 4: One of the very first experimental devices for polarography with the DME (on right side)

(Reproduced from the free access website; see ref. [6])

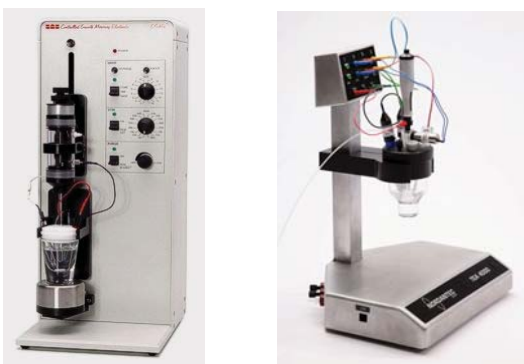


Fig. 5: Two modern constructions of the hanging mercury drop electrode (with controlled growth of the Hg-drop, left; miniaturised version, right)

(Illustrative photo images from the authors' archives)

Despite many times proven usefulness and reliability of these two liquid mercury-operated electrodes, the last decade is extremely unfavorable for both being fully in sign of their total removal from laboratories. And, again, despite the fact that, up until now, quickly renewable and ideally smooth surface as the main trump of the DME and HMDE configurations has not been rivaled or even approached by any other alternate sensor, including the latest hit in the contemporary electroanalysis – *bismuth-film plated electrode* (BiFE [9]) and related arrangements, having already achieved the firm position within a new family of *non-mercury metallic electrodes* [10].

On the other side, the replacement of a former leader among the reference electrodes — the saturated calomel electrode (SCE) — is already the reality and neither electrochemists nor electroanalyst will cry for. Its rather complicated and fragile construction with technical impossibility of miniaturisation are the drawbacks known for long time [8] and systematic removal of SCEs from labs in favor of a more flexible Ag/AgCl is now nearly completed.

- This contribution aims to review the scope of the occurrence and use of mercury, the truth and the myths about its toxicity, as well as other trivia associated with the present day's dampening of industrial use of this metal element, including some reflections of the above-mentioned mercuriophobia in public life. Furthermore, a number of objective facts on the toxicity of the individual forms of mercury and of its more frequent compounds (from less dangerous precipitates of the Hg_2Cl_2 and HgO type, *via* highly poisonous ionic forms of Hg_2^{2+} , Hg^{2+} and $\text{HgCl}_n^{(n-2)-}$, up to extremely toxic organomercury derivatives) are given in association with the real data and findings archived at the *Czech Toxicological Information Center (CTIC)* and concerning exposure to mercury in all its forms, with the corresponding reports on documented mercury intoxications.

Technical Notes

Methods for Determination of Mercury: A Brief Survey

Wherever reported below, the results on the contents of mercury had to be obtained by means of properly done quantitative analysis. At present, the analysts have at their disposal the whole arsenal of powerful instrumental techniques and their choice depends upon the form in which mercury is present in the sample and, of course, upon the actual concentration level. Consensually, the most frequent determinations of mercury are being accomplished with the aid of spectroscopic measurements [11]. Maybe, the most popular for this purpose is atomic absorption spectroscopy (AAS) applicable to the determination of mercury vapors, as well as of mercury in solid form from which the metal can be released and entrapped as the Au-Hg alloy – the gold amalgam.

This is also the case of special one-purpose devices, such as "TMA 254" or "AMA 254; both being developed and marketed in the Czech Republic [12]. Both apparatuses are highly effective, enabling to achieve extremely low detection limits down to $0.01 \text{ ng}\cdot\text{L}^{-1}$ Hg in water and solid samples, or around $0.1 \text{ ng}\cdot\text{L}^{-1}$ in urine and other biological fluids. However, the most efficient instruments utilize the principles of ICP-MS (or yet more efficient ID-MS) and ion chromatography; the latter allowing one to perform also *speciation*, recognizing the individual forms of Hg in one sample (*e.g.*, inorganic Hg_2^{II} and Hg^{II} salts, or strictly monitored organometallic compounds like methylmercury, CH_3Hg^+ [11]).

Finally, some electroanalytical techniques are applicable as well, mainly electrochemical stripping analysis (ESA [7,13]) which — thanks to the additional pre-concentration step — may offer sufficiently high sensitivity and selectivity, both at pretty low costs compared to the above-mentioned AAS, ICP- or ID-MS, and IC. In some cases, ESA can attain far below the nanomolar concentration level [14]. In electroanalysis as such, the determination of Hg^{2+} ions, Hg^{II} species, or some anions (*e.g.* HgCl_3^- or HgI_4^{2-}) is usually accomplished with the employment of gold electrodes [8,13,15]; advantageously, in the gold-film configuration, eliminating time-consuming electrode regeneration [16]. Widely applicable are numerous chemically modified electrodes (CMEs [17,18]) in combination with ESA, and surprisingly also some ion-selective electrodes and direct potentiometric indication [19]. Regarding the former configuration, very effective combinations can be obtained with *adsorptive stripping voltammetry* [20] – the technique invented and principally elaborated by **Professor Robert Kalvoda (28. 3. 1926 – 2. 8. 2011)**, to whom this review article is dedicated.

Data Collection at the Czech Toxicological Information Center (CTIC)

As stated above, the data concerning mercury intoxications were extracted from the special database (programmed in MS Access) of the calls to the CTIC in Prague, between January 1, 1995, and July 31, 2010. In each inquiry, the relevant data concerning the exposure were recorded according to the standard protocol, including: age and sex of the patient, time of the intoxication, estimated dose, symptoms of intoxication and whether first aid and any treatment has already been administered. In addition, the prognosis of the patient at the time of call was considered and, if needed, further managed with a therapy recommended. Finally, if a patient under investigation needed hospitalization, the discharge report from the hospital was required.

Mercury under Strict Control

Regarding the gradually suppressed use of mercury in the industry, the respective activities result in various restrictions and limitations, when *e.g.* it is prohibited to sell the body thermometers containing mercury and other similar devices (barometers, sphygmomanometers or tonometers [21]), the batteries and accumulators (containing more than 0.0005 % m/m Hg [3]), the button cells (with more than 2 % Hg [3]), and many other (mostly liquid) mercury-containing products and materials.

On the other hand, there is still a tolerance for the use and marketing of compact fluorescent lamps [22] with the mercury content below 5 mg Hg (per lamp,) straight fluorescent lamps for general purposes with the content below 10 mg Hg, tri-phosphate lamp with a normal life time with the content below 5 mg Hg, or some other illumination products with smaller amounts of mercury [21,22].

Notoriously known are also the efforts of many ecologists targeted on the ultimate removal of mercury from thermometers; *i.e.*, from a source containing only minimal quantities of the metal. On the contrary, almost the same people are very active in introducing the above-mentioned mercury-containing saving bulbs and fluorescent tubes loaded with considerably higher amounts of mercury.

Note: In 2011, the distribution of classical 60W- bulbs was prohibited; instead, the saving light bulbs having been introduced. It has already been confirmed that the energy-saving light bulbs are not as bright as their predecessors and the claims about the intensity of light produced were exaggerated. Moreover, these newly popularized bulbs contain high amounts of mercury; for instance, the usual 23W-saving light bulb (equivalent to classical 100W-bulb) contains 5-10 mg Hg [23]. In contrast to this, the equivalent (classical) 100W-bulb is totally mercury free; however, the amount of mercury released during production of electrical energy is about four times higher in case of classical bulb. Special processes to eliminate mercury in power plants have been developed for many years; but, only 10 % of all saving light bulbs is disposed ecologically; the rest comes into the municipal waste [23]. Moreover, it is necessary to take into account that mercury is present in the form of vapors in fluorescent tubes.

Therefore, in case of its accidental destruction, mercury is released in one of its most toxic forms and can be inhaled directly into human organism. In summary, as a consequence, the huge amounts of saving bulbs and fluorescent tubes being produced and used at present represent a new serious danger for the environment.

This can be well documented on the actual situation in some regions in the Czech Republic, when using the following report (from a local on-line newspaper [24]):

PRAGUE / BRNO ... The current ban to sell traditional 60W bulbs will force the hundred of thousands of (Czech) inhabitants to buy the new saving light sources. According to an estimate of the EKOLAMP agency, new saving bulbs are now used in 80% households. However, people are quite undisciplined, ignoring recycling policy, and the used bulbs end their journey at the landfills (see Fig. 6 above), representing more than 1,000 tons of waste glass, plastic material, various metals, and mainly – approximately 75 kg of highly toxic mercury...”



Fig. 6: *The saving bulbs in garbage* (Illustrative photo according to [24])

A brief excursion across the present day's hectic activities concerning the planned mercury ban can be concluded by quoting some maximal allowable limits for the content of mercury declared by international or local norms [25-27]:

- *Blood* ... Population level 4–10 $\mu\text{g}\cdot\text{L}^{-1}$; biological limit for workers limit in Czech Republic is not given, in USA population level 8 $\mu\text{g}\cdot\text{L}^{-1}$ and occupational limit in exposed workers 15 $\mu\text{g}\cdot\text{L}^{-1}$; in case of acute intoxications the levels are $> 95 \mu\text{g}\cdot\text{L}^{-1}$ [26].
- *Urine* ... Normal population level: 3–7 $\mu\text{g}\cdot\text{L}^{-1}$, biological limit in urine (for workers according to the Czech legislation) 0.1 $\text{mg}\cdot\text{g}^{-1}$ creatinine (0.056 $\mu\text{mol}/\text{mmol}$ creatinine) [25]. In the USA, population level $< 5 \mu\text{g}\cdot\text{g}^{-1}$ creatinine and an occupational limit in urine of exposed workers $< 35 \mu\text{g}\cdot\text{g}^{-1}$ creatinine (not provoked with a chelator) [26].
- *Air* ... Maximal allowable concentration: on average: 0.05 $\text{mg}\cdot\text{m}^{-3}$; ceiling: 0.15 $\text{mg}\cdot\text{m}^{-3}$, or 0.025 $\text{mg}\cdot\text{m}^{-3}$ in the USA (ACGIH) [27].

In connection with the data for mercury in air, it is worthy of mentioning that there also were maximal possible concentrations of Hg-vapors measured the in 1 m^3 of air for the different temperatures; specifically: 0°C ... 2 mg Hg, 20 °C ... 14 mg Hg, 100 °C ... 2420 mg Hg (after [14]); whereas the concentration of mercury in air evidently dangerous to health or even life is quoted to be 10 mg Hg m^{-3} (see ref. [26] and page 596 therein).

Mercury: Toxicological Profile of Its Forms and Compounds

As the toxicologists say, the actual doses are the most important. Nevertheless, the form is of comparable importance. The pattern and severity of toxicity are highly dependent upon the form of mercury and its pathway of exposure [26].

Toxicity of Liquid Mercury

Liquid metallic mercury is poorly absorbed from the gastrointestinal tract and the acute ingestion has been associated only with poisoning in the presence of abnormal gut motility, due to the markedly delaying of normal fecal elimination or, alternatively, after a peritoneal contamination. In any case, the liquid mercury is a heavy laxative [28,29].

Apart from these medical facts, the toxicity of the liquid mercury is a very often discussed topic [26-29], including the electrochemical forum. It is even possible that natural fear from liquid mercury had subconsciously contributed to very intensive activities associated with miniaturization of the mercury drop-based electrodes (see above).

Note: Herewith, it is useful to recall two rather bizarre examples of oral intake of liquid mercury, confirming that the risk of acute poisoning is indeed minimal. First, it is a story of unlucky love in the former Czechoslovakia [27], when a desperate girl voluntarily swallowed several grams of mercury. Instead of the expected death, she had recovered soon and, since then, became the wanted object of exhibition at medical faculties for several years, when the students and other university staff could observe — under a roentgen irradiation — how the mercury circulated in her blood system, including its passage through the pumping heart. The second case is then a criminalistic legend from the old Austro-Hungarian Empire [30], when a (never-revealed) joker had injected liquid mercury into bonbons that were subsequently distributed among the VIPs attending the famous ball at Vienna's Opera. According to the contemporary press, almost every infected victim had suffered from a strong diarrhea (almost demolishing the toilets), but no-one died or being otherwise seriously endangered.

Also, under a massive and uncritical influence of public mass-media (*e.g.*, some private TV channels in the Czech Republic), even the professional staff may behave inadequately while confronted with an accident concerning the sudden appearance of liquid mercury. To illustrate this (exemplary case of mercuriophobia), the following footnote brings a report published recently in a local press in Northern Moravia [31]:

Note: OPAVA – Fire fighters in helmets running from side to side, crowds of people gazing around, pedestrians crossing their ways between two fire trucks. In this way, one can describe the havoc in the streets of Opava, on Monday, after 10 a.m., and nearby the skyscraper of the Ministry of Agriculture. Reason? Danger of poisoning! In the fourth floor, inside kitchen, some droplets of unknown substance have been found on the floor. According to the spokesman of the Opavian Police: „It seems this is mercury that, in extreme cases, may be deadly toxic“. An amount of 0.02 deciliter of this substance has been collected and sent to be analyzed. The crucial is, however, to find out how and why liquid metal appeared in the building,” he explains, adding yet: “We are just investigating if there is anybody who placed it there intentionally. To reveal this, the police will appreciate any information which would lead to close the case...”



Fig. 7: The fire brigade in Opava ready to collect 2 mL Hg..

Toxicity of Mercury Vapors

Inhalation of Hg-vapors by lungs is practically complete. The acute inhalation of high concentrations of metallic Hg-vapors may cause severe chemical pneumonitis and non-cardiogenic pulmonary edema [28,29].

Chronic intoxication from inhalation of mercury vapor produces a classic triad of tremor, neuropsychiatric disturbances, and gingivostomatitis [26].

Due to high solubility in fats, Hg-vapors come into brain circulation in few minutes. They cross hematoencephalic barrier, acting neurotoxically. It is expected that, in brain tissue, elemental mercury is oxidized to Hg^{II} and these species cross the hematoencephalic barrier being then accumulated in cortex and basal ganglions. Similarly, mercury can be transformed by catalase to Hg^{II} in erythrocytes and this divalent form is then distributed into tissues, interacting readily with the $-\text{SH}$ groups in the enzymes. The highest depot is present in kidneys; usually, in adrenals. The kidneys tissue reacts by producing metallothioneins (MTs; cysteine-rich proteins [32]) which effectively bind mercury. As a consequence, kidney — namely: proximal tubulus and glomerulus — are badly damaged after such saturation.

It is evident that the occurrence of Hg-vapors must be minimized. The incinerators, where the products containing liquid mercury are combusted, have been and may yet be the source of the Hg-vapors. Therefore, the products of everyday use — mainly, the batteries containing up to 1 % Hg or some fluorescent tubes — have to be sorted out and, in this way, excluded from this thermal destruction. Another source of considerable amounts of liquid mercury, industrial electrolyzers (used *e.g.* in production of Cl_2 and NaOH) are now being replaced by liquid mercury-free devices.

To prevent the release of the Hg-vapors, the waste liquid mercury should be stored under column of water in a closed bottle. The thin column of water is not able to block the evaporation of mercury from the surface. A 5-cm high water column decreases the amount of mercury vapors negligibly; 10-cm high column suppressing the rise of the vapors down to 75% compared to a free mercury surface.

Note: If the mercury pool is placed on the floor, the concentration of vapors in air (considered to be measured 1 meter above the floor), corresponds to the hygienic standards under normal room temperature ($25\text{ }^\circ\text{C}$) and in the height of 1.8 m their level is deep below hygienic standards due to high density of mercury. Nevertheless, the evaporation increases with the increasing room temperature and the surface of evaporated mercury. Our results are in good agreement with experiments described by Waldman et al. [33], where evaporation of mercury from broken thermometer (about 1 g of metallic mercury) was followed in a typical room contaminated with the liquid mercury. Two modifications were investigated: 1) room with floor convector near to glass wall; 2) room with glued carpet. In the first case, the concentration of mercury levels amounted to $30\text{--}60\text{ ng.m}^{-3}$ about 50 cm above the convector, $140\text{--}400\text{ ng.m}^{-3}$ on the upper edge of convector, and $1\ 400\text{--}4\ 000\text{ ng.m}^{-3}$ in the center of convector. In the other case, the level of mercury vapors was $20\text{--}40\text{ ng.m}^{-3}$ approx. 1.1 m above the contaminated carpet; $50\text{--}100\text{ ng.m}^{-3}$, and $800\text{--}15\ 000\text{ ng.m}^{-3}$ closely to the carpet.

Toxicity of Amalgams

The various *amalgams* — in a shortcut, the alloys of mercury with other metals — are present in human life for many hundred years; *e.g.*, as amalgams used in dentistry (mainly with silver), in mining industry (with gold) and, recently, also in voltammetry as relatively new electrode material [34,35] and one promising non-toxic alternative to mercury.

In case of amalgams, many fears were introduced by non-specialists. Probably, the source of such incorrect information could be derived from a wrong hypothesis that the amalgams are pasty and incompact mixtures of liquid mercury with solid particles of other metal(s), from which the mercury can readily be released. However, there is an indirect way of intoxication from amalgams connected with historical mining of gold and silver; both being based on amalgam formation.

Note: Reportedly [27], mercury amalgamation was firstly applied to silver ores with the invention of the so-called patio process in Mexico (Bartolomé Medina, in 1557). Yes, this way of mining seems to be highly dangerous for the environment: gold ore was mixed with mercury, forming amalgam which was subsequently burned in fire and mercury thus released into environment. The Spanish Empire transported mercury from mines in d'Almadén (see Fig. 2 and note beneath) across the Atlantic Ocean to supply their silver mines in Zacatecas and Potosí. Another source for mercury in the Spanish Empire was the mine of Huancavelica in Peru (discovered in 1563). Some century later, in 1648, the viceroy of Peru declared both Potosí and Huancavelica as "the two pillars to support his kingdom and the Spain". It can be added that this way of gold and silver mining is applied to date; at least, in some developing countries.

The other sources of mercury release from amalgams are crematories. There, the amalgams are destroyed by combustion of human bodies and the Hg-vapors are deliberated into the atmosphere. However, the application of special filters solved this problem [36].

On the other hand, the silver amalgams used as dental fillings can be seen, from a toxicological point of view, as almost nontoxic [1,29]. Nevertheless, there are still certain voices claiming that mercury may slowly leach from these alloys and can thus be accumulated in the body. As shown overleaf, these rumors can simply be dispelled by recent findings.

Note: The first people who used amalgams to fill cavities in decayed teeth were the Chinese in the 7th century. In modern history, the first successful experiments with dental amalgams were performed and described French dentist *Auguste Taveau* [1]. In 1826, he had developed a dental amalgam from silver coins and mercury by preparing a medium rigid paste which he loaded into a tooth and shaped it as required.

Taveau's fillings were cheaper than the gold leafs used at that time; moreover, they were better manipulated. His amalgam was low in the mercury content and had to be heated in order to dissolve the second metal at an appreciable rate. However, it exhibited also some disadvantages. At first, this type of amalgam augmented markedly its volume during solidification. (Today, this expansion process is considered to be rather advantageous enabling to fix firmly the amalgam in the cavity.) Then, Taveau's fillings tended to stack out from the tooth, which complicated the



Fig. 8: *The dental amalgam*
(Illustrative photo taken from authors' archives)

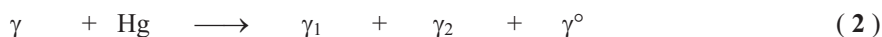
proper occlusion.(At that time, the amalgam-polishing tools were unknown.) And because teeth could be ripped by internal stress, Taveau's "silver paste" did not receive good reputation.

The first modern dental fillings were introduced by brothers Crawcour's in New York. Very interesting, in comparison with today's environmental trends, are the complications which accompanied introduction of dental amalgams. They were charged by other dentists with amorality and professional incompetence, charlatanism, and applied material which these brothers used for dental filling was impeached. It was declared that amalgam is not suitable for dental fillings, because it is harmful and therefore it cannot be placed in human mouth. It was emphasized that mercury volatilizes from the filling gradually and it is harmful for human organism. Due to these attacks the brothers Crawcour's had to leave New York. Since then it was not possible to use amalgam by any prestigious dentist. The illnesses with unknown causations were ascribed to the amalgam fillings (paralysis of limbs, throat diseases, even tuberculosis, *etc.*). In 1843 representatives of American Dental Association (ADA) prohibited the use of amalgam generally. Some dentists were proscribed from the ADA, because they publicly used amalgam. About 1870, one of the most famous American dentists - Joseph Foster Flag declared for the application of amalgam. He has proven that after many years of experiments with this alloy, the teeth filled by amalgam have a longer durability in comparison with other fillings, including gold. The amalgam alloys have been the most frequently used type of fillings since the end of 19th century [1].

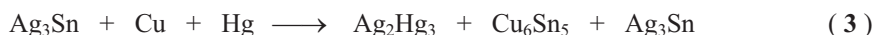
Indeed, the amount of liquid mercury released from amalgam fillings is negligible. The reason lies in the fact that the most part of the dental filling is formed by the solid crystallite, an adduct Ag_2Hg_3 , being denoted as " γ_2 -phase". Traditional amalgams, prepared according to the standards (valid before 1986 [1]), contained more than 65 % Ag and less than 6 % Cu. Besides the mercury itself, the initial compound was a binary Ag_3Sn used in an excess. Afterwards, the main reaction, occurring during the amalgam formation, can be described as follows:



or, when using special symbols,



where "x" is 7-8, and the Ag_3Sn is in sufficient excess; hence, it can be written on both sides. The ISO standard № 1559 was introduced in 1986 [1], in which the content of silver was decreased down to ca. 40 %, while the percentage of copper increased up to ca. 30 %. The respective reactions are then as follows:



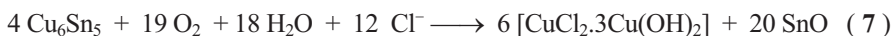
where Cu_6Sn_5 is the " η -phase" and Cu_3Sn the " ε -phase". The temporary intermediate (existing from days to weeks), product " γ_2 ", then reacts with copper to form Cu_6Sn_5 . Thus, a minimal amount of free mercury is present in copper-enriched alloy.

Furthermore, in case of amalgams, a *tarnishing* and *the corrosion* are often confused by non-specialists. The tarnishing means the loss of lustrous surface of a metal or an alloy, when the original surface is hidden beneath a compact coat. After this transformation, however, the alloy integrity is not affected and no change in mechanical properties expected.

On the other hand, the corrosion of dental amalgams as qualitatively different process can be described in this way [37]:



The released mercury can react with abundant Ag_3Sn to a newly formed " γ_1 phase" or can enter the alimentary tract. In the case of copper-enriched alloys, one has:



Therefore, in copper-enriched alloys, the amount of released mercury is substantially decreased. (Yet another decrease can be attained by adding palladium into the mixture; usually, at a ratio of $\text{Pd} < 1 \%$ [37]). According to the WHO, the amount of released mercury from dental fillings in mouth ranges between 1.2 and 29 $\mu\text{g} \cdot \text{day}^{-1}$, which corresponds to the usual intake from food (2-5 $\mu\text{g} \cdot \text{day}^{-1}$), and being practically negligible compared to the exposure from ambient air (32 - 96 $\mu\text{g} \cdot \text{day}^{-1}$) or from a workplace (about 430 $\mu\text{g} \cdot \text{day}^{-1}$).

The preparation of dental amalgams represented some danger in the past. Few mild chronic mercury intoxications of dentists after long-term careless handlings with amalgams have been reported (due to preparation of the amalgam with the unprotected fingers, mercury could be absorbed through the skin pores; see again [37]). Later on, this danger has been minimized by introducing the automated mixers.

Note: Apart from the above-discussed little harmfulness of dental amalgams, there have been some precautions introduced believed to reduce the risk of pollution with mercury [1]:

- ✓ ... The use of encapsulated materials;
- ✓ ... Preparation (trituration) of amalgams (capsules) in special devices – amalgamators;
- ✓ ... To store excess, waste or scrap amalgam under water or under chemical fixative solution in a sealed container;
- ✓ ... Proper flooring without any (or with minimal) joints;
- ✓ ... The capsules should be opened away from the face in well-ventilated conditions;
- ✓ ... Effective air conditioning or ventilation;
- ✓ ... Under normal service conditions, amalgam restorations are covered by a film of saliva. This reduces the vapor pressure significantly and reroutes largely the mercury from the respiratory to the GI tract where the absorption of mercury is markedly lower;
- ✓ ... Avoiding higher temperature as vapor pressure increases dramatically with increasing temperature.

Toxicity of Inorganic Compounds of Mercury

In general, the inorganic compounds containing mercury are considered as highly toxic. Nevertheless, it is necessary to differentiate among the soluble salts; *e.g.*, HgCl_2 , $\text{Hg}(\text{NO}_3)_2$, or $\text{Hg}(\text{ClO}_4)_2$ and insoluble substances, *i.e.* precipitates, like Hg_2Cl_2 , $\text{HgO} \cdot n \text{H}_2\text{O}$, HgS , *etc.* Thus, for instance, the (oral) lethal dose of *calomel* (aka "white precipitate"; Hg_2Cl_2) amounts between 2-3 gr., whereas notoriously known "sublimate" ("mercuriochloride", HgCl_2) may kill in the amount of 0.2-1.0 gr., which is close to a lethal intake of $\text{Hg}(\text{NO}_3)_2$ being 0.4-2.0 gr.

Regarding the poisoning as such, a treatment with special *chelating antidotes* may be highly effective, depending on the dose and time latency since the ingestion [28]. One of the most known is *BAL* (*British Anti-Lewisite*, aka *Dimercaptol*; 2,3-dimercapto-propanol), a compound developed during World War II. (Amusingly, perhaps the most effective antidote would be *alkaline cyanide* [30], forming extremely stable and non-dissociated molecules of $\text{Hg}(\text{CN})_2$; but, to date, there has been no-one who would have seriously tried such a cure.)

Toxicity of Organometallic Compounds

Organometallic compounds (in general: R–HgX, R–Hg–R', or Ar–Hg–Ar, where "R, R', and Ar" are the respective alkyls or aryls (typically, CH₃, C₂H₅, and C₆H₅) and "X" is an anion like Cl⁻, NO₃⁻, HSO₃⁻, or HSO₄⁻) are extremely, almost deadly toxic. Especially, the latter is the case of methyl mercury, CH₃Hg⁺, as a readily bioaccumulable species. (Due to its relatively small but molecule with lipophilic alkyl-chain, CH₃Hg⁺ ion is soluble in fats and capable of penetrating through the hematoencephalic barrier in brain and [28,29].)

In case of organomercury compounds, the efficacy of chelating antidotes is not sufficiently proven and very low doses can be lethal [1,38,39].

Note: A text-book case is the accident in Japan (at Minamata, in 1953 [1,27]), where more than 100 fishermen were exposed to mercury, originally (and secretly) released from near factories to the sea and then bio-transformed to methyl mercury. As a result, 40% of them died, a major part of the surviving persons was incapacitated, having had locomotion problems, often with the loss of eyesight (or with a tunnel-vision), and also becoming the hearing impaired or even deaf.

Also, the utilization of the mercury-containing vaccine *Thiomersal* has been minimized during the recent years [39] and, at present, *DMPS* (aka *Dimaval* or *Unithiol*; 2,3-dimercaptopropane-sulfonate) is the chelating antidote of choice. Compared with the previously used and above-mentioned *BAL* (*Dimercaptol*), it offers many advantages, such as lower toxicity and the availability in both oral and parenteral preparations. Also, more is known about the pharmacokinetics of *DMPS* (given *per oral* or *in vitro*) in the human body than about any other dimercapto-based chelating agents. Yet another possibility is the application of *DMSA* (2,3-dimercaptosuccinic acid, a succimer [5,40-42]).

Poisoning with Mercury: Survey of Symptoms and Related Medical Observations

Clinical Presentation. Acute inhalation of high concentrations of metallic mercury vapor may cause severe chemical pneumonitis and noncardiogenic pulmonary edema [1,28,29]. Acute gingivostomatitis may also occur. Chronic intoxication from inhalation of mercury vapor produces a classic triad of tremor, neuropsychiatric disturbances, and gingivostomatitis. Acute ingestion of inorganic mercuric salts causes an abrupt onset of hemorrhagic gastroenteritis and abdominal pain. Intestinal necrosis, shock, and death may ensue. Organic mercury compounds cause paresthesias, ataxia, dysarthria, hearing impairment, and progressive constriction of the visual fields.

Inhalation. To diagnose the development of acute pneumonitis and pulmonary edema, observations for several hours and supplemental oxygen is needed [1].

Ingestion of Mercury Salts. Due to a severe gastroenteritis with a fluid loss, aggressive treatment of shock with intravenous fluid replacement is of utmost importance. Vigorous hydration may also help maintain urine output. Acute renal failure is usually reversible, but hemodialysis may be required for 1-2 weeks.

Ingestion of Organic Mercury. A symptomatic supportive care is necessary.

Allergy to / from Mercury. At the end of this paragraph, it is necessary to quote the danger concerning an allergy to mercury which can be registered in behavior of some patients (about 1 to 4 % of population [43]).

In medicinal and clinical literature, the experts distinguish among the allergic reactions. The type "I" is very rare and reported *e.g.* after preparation of dental filling. The most frequent is allergy of the type "IV", the so-called delayed type, being described also as a hypersensitive reaction [43].

Poisonings with Mercury and Mercury Compounds Archived at the Czech Toxicological Information Center (CTIC) within the Period of 1995-2011

Annually, the CTIC receives from about 120 to 150 phone calls regarding intoxication with mercury in all its forms. (This value represents *ca.* 1.5 % of all inquiries registered therein.) People — typically, small children —, had been exposed mainly orally (about 87 %), after they have eaten "shiny and attractively looking small balls" of liquid mercury from broken thermometers. Per rectum exposure (about 2 %) occurred due to accidental breaking the thermometer during the measurement. Potential or real exposure to mercury vapors (liquid mercury on the floor) was reported in about 8 % of all inquiries. The suicide attempts using mercury or its compounds were very rare.

In average, per a year, two individuals (here, "subjects") ingested a mercury salt, five subjects swallowed metallic mercury and (statistically) less than one patient injected liquid mercury to his/her body intramuscularly or intravenously. The number of occupational symptomatic intoxications was low at least for three decades - only 18 professional intoxications were reported by the *Institute of Health Information and Statistics*, Czech Republic, in the years of 1973-2003.

Case Reports from the CTIC

As already mentioned, often repeated are the inquiries dealing with broken thermometers in the room, in tea pot, in rectum, *etc.* In the following paragraphs, some of the most remarkable reports on **ingestion of metallic mercury**, archived in the shelves of the CTIC within the period of 1995 -2011 are surveyed, including the inevitable details:

- 10-month old boy had a broken thermometer in the rectum as he fell during the temperature measurement, a perforation of the rectum wall to the proximity of the urethra resulted in a deposit of Hg and an abscess. The metal was removed by surgery, the serum applied increased the content of Hg in blood to a 4-fold level and decreased to a 2-fold level within three years of follow-up, without further chelating treatment.
- 48-year old man drank a part of 10 mL of liquid mercury in his beer, being admitted with the signs of inebriation, and Hg in urine with 2.23 $\mu\text{g}\cdot\text{g}^{-1}$ creatinine; *i.e.*, normal population level.
- 17-year old woman drank 1-2 mL of mercury, soon she developed diarrhea and discomfort in the abdomen, her friend has seen droplets of Hg in the toilet. She was nervous but denied a suicide attempt (even though if she already committed several).
- 27-year old man got a sting from an unknown attacker into the forearm, two days later he developed pain and twitching sensations in the forearm, edema, and elevated body temperature (37.5 °C), a repeated drainage with Hg leak was performed, and antibiotics prescribed. Blood Hg exceeded the population limit 14x.
- 22-year old man injected 2 mL of metallic Hg into his left cubital vein; he developed inflammation and pain in the cubital region. The content of mercury in urine was very mild increased (seen *via* 0.00039 $\mu\text{mol}\cdot\text{mmol}^{-1}$ creatinine) compared to the population level.
- 18-years old woman, drug-user, injected mercury from one thermometer paravenously into her forearm. Three months later, she had had tingling and pain in the hand. The skin around the needle injection was corny and round.
- Rescue group of firemen liquidated the spilled mercury in a grammar school. According to the fireman spokesman, the total volume of mercury (brought by one of the students) amounted to 50 mL. Pupils were evacuated of the building and the area of about 30 m² was cleaned subsequently. The rescue action was realized under the cooperation of Prague Police, Prague Fire Brigade, and a special team of Prague Transport Organization.
- The subway station was closed for two hours due to mercury dropped on stairs and in the vestibule (total amount: 100 mL). The firemen removed the metal by special air pump.
- 58 year-old technician had broken down an ambulatory barometer (for measuring of gas pressure in the pipeline), containing 3,500 mL Hg in its van (!), and the liquid spilt on the floor. After 4 hours of tiny watch-work, he succeeded to fill up the device back and repair it (!!).

However, after other 4 hours of sleep in the living-area of the van, he had woken up with cough, chills, dyspnea and consequently, with chemical pneumonitis and mild lung edema was seen on the chest radiograph. He was treated symptomatically and recovered fully, without the need of chelating treatment [39].

- Four members of a family were severely exposed to mercury vapors while cleaning a Persian carpet polluted by liquid mercury. The most severe symptoms were seen at the father (35 years old) – gingivitis, bronchitis, headache, tremor, nervousness, sleeping disorders; mother (36 years old) – headache, vertigo, gingivitis; daughter (6 years old) – acrodynia; only the son (16 years) was asymptomatic. Urine Hg-level $1.86 \text{ mg}\cdot\text{g}^{-1}$ creatinine in the father exceeded 20-fold the biological exposure limit for the workers and blood Hg-level in the mother (0.770 mg/l) 150-fold the normal population level. All persons intoxicated were treated with DMPS in capsules for 6 weeks. The highest excreted amounts of mercury were recorded in the father. All members of the family had fully recovered [44].
- 45 years old woman filled electrodes by liquid mercury for two working days in a room with poor ventilation. The working table was about 40 cm below her face, the room temperature about 40 °C. She developed nervousness, tremor, and metallic aftertaste in mouth. She recovered fully within a few days without any further treatment.

Similarly, a selection from the reported cases on **intake of inorganic mercury salts**, coming from the same source, is described in the following lines:

- 21-year old man used during three weeks 50 g of an cosmetic ointment with 10% mercury amidochloride ($\approx 4 \text{ g Hg}$). Extreme tiredness and fasciculations on the extremities appeared after the end of the ointment treatment. Nephrotic syndrome and hypertension were diagnosed 1 month later; a hypertension developed which needed the treatment with 3 antihypertensives. Two months after the ointment application the patient was very weak with tremors of the hands, almost unable to walk, and had lost 20 kg of body weight. He had severe neurasthenic symptoms and his behavior suggested acute psychosis. The patient had proteinuria of up to 11.10 g/24 h, and renal biopsy revealed diffuse membranous glomerulonephritis. Treatment with DMPS was started and mild clinical condition improvement was seen within 2 weeks. Further follow-up has shown slow normalization of renal functions. After 1 year, proteinuria decreased to 0.62 g/24 h and body weight normalized, and the antihypertensive treatment could be omitted. Neuropsychological, electromyographic and kidney function findings became almost normal within two years of follow-up [45].
- 63-year old man, put by mistake a lethal dose of HgCl_2 into his coffee instead of sugar (!) After the accident, he washed his mouth; however, not having informed the doctor. On the following day, he developed anuria, vomited repeatedly bloody gastric content, had black stools, he was exhausted and had corrosive stomatitis with several ulcerations. He was treated with DMPS and hemodialysis, within one week kidney failure improved to polyuric phase; however, temporarily, therapy of his hypertension had to be intensified.

Mercury: The Current Situation in Physical and Chemical Laboratories

Naturally, the gradually growing aversion against mercury at all the fronts could not omit the physical and chemical laboratories equipped with electrochemical analyzers in combination with the mercury electrodes.

Mercury Drop-Based Electrodes and Related Configurations

Obviously, the most abundant representatives of these configurations are the already presented Heyrovský's (i) **dropping mercury electrode (DME)** [5]; see Fig. 4) and, mainly, the (ii) **hanging mercury drop electrode (HMDE)**, [5,46-54]; *syn.* static mercury drop electrode SMDE *, occasionally replaced by modern modifications or minivariants (Fig. 5) offered nowadays by renowned manufactures.

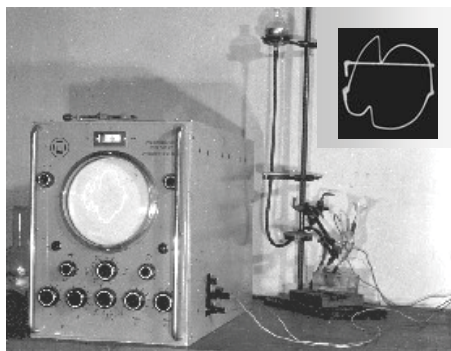
*) **Note:** Model "SMDE-1", made in Czechoslovakia (by *Laboratorní přístroje Prague, a.s.*), is well-known to minimally two generations of Czech and Slovakian electrochemists. Besides quite popular and well-serving analyzer from the same manufacturer, model "PA-3", (please, do not confuse with its successor, model "PA-4"), the "SMDE-1" product was a pretty forgery. Being designed as more-or-less separate stand in the three-electrode arrangement, this failed version of the HMDE has become legendary as a device whose reliability and lifetime could be counted in weeks; maximally, few months. Then, "originally" designed — and, apparently, even patented — mechanism for controlled closing (of the upper mouth of capillary with a needle valve) started to hamper until it got totally out of order. Since then, the user of the SMDE-1 stand(s) had had two possibilities. (1) Had he chosen to repair the damaged instrument by himself, he risked an accident with spilled mercury and its cleaning as described above. However, (2) had he decided to ultimately dismount all the liquid-mercury operated compartment, he obtained a robust and well-functioning electrode cell for experimentation with alternate working electrode(s); in addition, with finely adjustable propeller (and later also with specially integrated unit for automated purging with inert gas). And as the author of this gloss can remember, almost each SMDE-1 stand he ever saw during his scientific career had ended in that way, having served much better in the adapted form; often, for lengthy years...

Historically, there are also further liquid-mercury operated electrode constructions, such as (iii) **streaming / jet mercury electrode** for (oscillo)polarographic measurements (SME, see *e.g.* [55] and Fig. 9 oveleaf) or (ii) **mercury pool electrodes** {MPEs; usually provisory arrangements with very large surface (up to 20 cm²)} for special voltammetric measurements [56], potentiostatic coulometry [57], or electrolytic cleaning of water samples [30].

Fig. 9:

Contemporary device for alternating-current oscillopolarography with the streaming (jet) mercury electrode, S(J)ME
(The electrode is depicted on right with upper insert showing an AC-polarogram)

(Illustrative photo reproduced from the free access website [6] and additionally edited)



Note: Regarding classical constructions of the DME (or SME), where one has to manipulate larger amounts of mercury, there is — of course — a certain risk of intoxication with Hg-vapors. For instance, it can happen by carelessness of the user who forgets to fill the reservoir (already filled with mercury) additionally with water that floats in heavier metal, forming thus a (liquid) lid that normally hinders the evaporation of mercury. Or, it can happen that the reservoir itself is broken down; *e.g.*, during careless re-filling. In this case, mercury is disintegrated into small droplets, tending to rapidly evaporate, and the spilled metal must be promptly collected. Practically every electrochemist once met such a situation, knowing well that there is no need for panic because he can effectively clean the splintered mercury by using spatula(s) from zinc or copper. Both are readily amalgamated and, thanks to this, the individual drops and droplets can be collected very quickly. When doing so, it can be viewed how some drops start to move (or even shake) themselves as soon as the spatula is in contact. And, suddenly, the drop completely disappears like being sucked inside [58]. This is nothing but just a confirmation of pretty high efficiency of the whole amalgamation process...

When considering deeper both basic types of mercury drop-based electrodes with the risk of employing liquid mercury, also the following features can be highlighted:

(1) At present, DME, SME, and MPE are used only sporadically; maybe, at few specialized institutions in one country / region and hence, even somewhat larger quantities of mercury required for their functioning does not seem to be problem from an ecological point of view.

(2) As already emphasized, modern constructions of HMDE need only minimal amount of mercury (see again Fig. 5) and even more abundant employment of such devices inside one institution / locality may not represent a serious danger.

In both cases, the amounts of mercury to operate these electrodes are still far below the loads typical for industrial use or the production of consumer goods (*e.g.*, saving lamps). This fact should be taken into account and if any restrictions in use of mercury are to come, chemical labs would be one of the last targets.

Despite the above-summarized facts, the unfriendly insight at mercury electrodes remains a reality. The individual innovations have been almost unnoticed, argumentation on their safe operability and reliability questioned. And the avers stays on. Shortly speaking, the mercury electrode has become one of the signs of old times in science.

It is indisputable that such opinion is now still more pronounced also amongst electrochemists and electroanalysts themselves. To be fair, it should be added that there is a very wide and diverse spectrum of voices that could be heard at recent conferences, meetings, seminars, or various panel discussions (see Fig. 10). Some of them advocate mercury, some are against, some call for tolerance, the remaining then balance somewhere in-between; nonetheless, all together falling into the following categories:

- (I) **Conservatives** always argue by the uniqueness of mercury as the (best) electrode material and do not admit any discussion or even compromise (e.g. to combine traditional principles with some findings from newest technologies).
- (II) **Pessimists** are those who somehow respect the latest trends, but openly doubt about their meaningfulness and distrust in alternative ways. In fact, also this group prefers mercury electrodes, but behaves according to a phrase “*Never say never...*”;
- (III) **Skeptics** are lesser pessimists, but sharing most of their features. In some respect, they hesitate about possible co-existence of both mercury and non-mercury electrodes, predicting a misty future for the electrochemistry as a whole.
- (VI) **Stoics** represent somewhat outstanding group being indifferent to turbulent events around mercury; often, because of the naked fact that their research interest is completely out of area concerning the development of electrodes and sensors.
- (V) **Realists** respect fully the latest movements, but — in contrast to the groups III — they are willing or even open to absorb new information. As a result, realists are flexible and capable of effectively combining all major advantages of mercury with positive features coming from new “non-mercury electrochemistry”...
- (VI) **Optimists** form a scientific society quite similar to the group V; a certain nuance being between the ratio of “mercury versus non-mercury orientation” in favor of the latter.
- (VII) **Enthusiasts** can be characterized as a particularly optimistic wing, devoting their attention to both mercury and non-mercury electrochemistry, with the actual inclination to one or another after prevailing mood in the society. Their elasticity is often remarkable.
- (VIII) **Activists** are those who openly or even militantly challenge the community to end the era of mercury electrodes in all the existing forms. Due to a nearly-centenary tradition of mercury electrodes that — in any respect — had to touch practically every electrochemist, it is believed that this community is represented by the individuals only; especially, in Czech Republic, in the fatherland of Jaroslav Heyrovský.

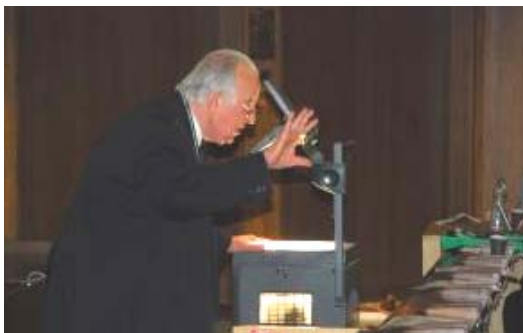


Fig. 10

Mercury, mercury electrodes, and polarography as topics of scientific discussion...

Above: Professor Petr Zuman gives his plenary lecture at the ESEAC Conference in Prague, 2008 (for details, see [59]).

Below: Similar presentation* by Prof. P. Zuman a decade ago, at the International Conference in Seč (near Chrudim), 1999.



(Photos from the authors' archives)

*) This lecture exists also in the full-text version and under title "*The use of polarography in the initial stages of investigations of organic electrode processes in aqueous solutions*" is available as a review article (see *Literature*, ref. [60])

Mercury Drop-Based Electrodes: The State of the Art. Thanks to a long tradition of both fundamental configurations, the DME and HMDE, their contribution to both theoretical and applied electrochemistry can be mapped in very detail [8,59-62] and, herein, only a short survey can be given.

- The DME with periodically renewable surface, is the integral part of polarographic instrumentation and this statement says almost all; nevertheless, the most typical achievements and possibilities in modern electrochemistry and electroanalysis can be summarized as:

(i) Tremendous theoretical apparatus and the respective archives of experimental data; both being unprecedented when considering any other electrode or detection system.

(ii) Continually renewable Hg-drops with almost ideally smooth surface and the exactly defined geometry allow one to carry out a great variety of polarographic experiments – from simple studies on the basic electrode reactions, via numerous advanced investigations of multi-step electrode mechanisms and after / consecutive reaction pathways, up to highly sophisticated measurements of some specific phenomena of either faradic or non-faradic character [59,60,63].

(iii) Less well-known but very useful is *preparative polarography* for studying of some intermediates formed during electrolytic reductions and scarcely obtainable in another way.

- Similarly, the stationary mercury drop configuration, *i.e.* HMDE, is renowned due to:
 - (i) High reliability and a wide flexibility of the HMDE is widely recognized and reflected in essentially endless palette of practical electroanalytical methods / procedures / protocols for the determination of various inorganic ions and molecules, organic pollutants, and pharmaceutically and biologically important compounds [8,61,62].
 - (ii) Again, less obvious but effective is the applicability of miniaturized HMDEs in flowing streams in the form of selective electrochemical detectors (*e.g.*, in wall-jet configuration) for FIA, HPLC, and capillary electrophoresis.

Mercury Amalgam-Based Electrodes

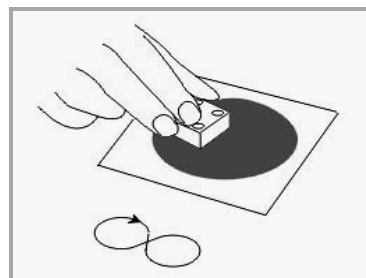
One of the most typical examples in consecutive replacing the (pure) mercury electrodes is connected with introducing the **amalgam-based electrodes** (see *e.g.* [34,35] and refs. therein); in this case, not only working or indicator electrodes, but also the reference as an alternative to the traditional SCE [64]. For electrochemists, these efforts are mostly sympathetic, but wider scientific auditorium sees the term "amalgam", still evoking the use of mercury.

In some respect, the latter are right – they will always argue that amalgam needed for these electrodes has to be first prepared, for which the use of mercury is, of course, inevitable. And similarly to the matter of miniaturized HMDEs, they would not want to hear the contra-arguments that the amount of mercury for such amalgams may be even negligible [34,35]. Thus, despite the fact that, in the area of amalgam-operated electrodes, there have been remarkable achievements with a long string of various construction variants (*e.g.*: Ag/Hg- and Cu/Hg-amalgams, polished- (see Fig. 11), film-like, Hg-meniscus operated electrodes, *etc.* [65-75]), this family of electrochemical sensors will apparently remain in the position of interesting, but only occasionally choices among a plethora of mercury-substituting and mercury-free electrodes and sensors (see *e.g.* [76-83]).

Fig. 11:

Polishing of Au/Hg-amalgam electrode designed as a flow-through cell for measurements in flowing streams.

Below: A trajectory for polishing recommended by the manufacturer to perform the operation on a special pad. (Illustrative picture; from authors' archives)



Mercury Film-Plated Electrodes and Related Arrangements

Retrospectively, the introduction and later intensive propagation of the so-called **mercury film electrodes (MFEs, [8,13,84-87])** represents, so far, the most successful attempt to replace mercury drop-based electrode and, mainly, the HMDE configuration. These film configurations are functioning *via* elemental mercury as well; but, in fact, one does not come into direct contact with the metal, because its *very thin layer* (the film) is being deposited onto a suitable electrode substrate — far most popular is the glassy carbon electrode (GCE) in the disc configuration (see also Fig. 12 overleaf and ref. [88]) — by potentiostatic electrolysis — either from special plating solutions [13,85] or directly in the sample and simultaneously with the analytes to be determined (*in-situ* arrangement [84]).

The film, obtainable by reducing a suitable Hg^{II} salt in the (sample) solution, is so thin (typically, below 1 μm) that it is viewed as a grey / black coating, whereas its genuine appearance is completely different — it is a fine ensemble of more-or-less consolidated tiny Hg-droplets distributed over the surface of the substrate electrode, when being observable merely with powerful microscopes (see Fig. 1B). Nevertheless, even such a unique structure behaves in the same way like elemental mercury and, in principle, mercury film electrodes can be employed for the same measurements as traditional constructions of the HMDE.



Fig. 12:

Glassy carbon rods from a portfolio of a manufacturer are the primary material for the GCE; consensually, the finest substrate for laboratory preparation of MFEs

(Illustrative photo withdrawn from the free access website; see [88])

Compared to them, there are some distinct differences [86,87]; most of them making the MFE particularly useful in electroanalytical practice: **(i)** MFE is mechanically more stable and can thus be used in the rotated arrangement or for field / outdoor monitoring in combination with portable analyzers; **(ii)** due to a very thin layer of mercury, the signals in ESA are sharper and usually better evaluable; **(iii)** due to the same reason, the sensitivity of measurements at MFEs is usually higher than comparable experiments with the HMDE; **(iv)** once again, because of extreme thinness of the Hg-layer (in some cases, expected to be

formed by monolayers), the formation of amalgams is more effective than at the "macrodrop" of HMDE, giving rise to the more pronounced interferences at MFE from alloying metals, as well as from some intermetallic adducts; finally, (v) principal difference in the surface microstructure if one compares the array-like character of mercury films, when the distribution and size of the individual droplets depend on some experimental conditions, with nearly ideally smooth Hg-drops. (Some sources claim [8,86] that the latter is also behind somewhat better reproducibility of measurements at HMDE, and its notably higher affinity to adsorb larger molecules, including DNA [89].)

Otherwise, quite similar feature for both HMDE and MFEs is simple and quick mercury renewal that, in the case of MFEs can be accomplished either electrolytically (by re-oxidizing the deposited Hg-droplets back to the Hg^{II} species during the anodic scanning) or even mechanically – by manually wiping the film off of the surface of the inert substrate using a filter paper or piece of a soft-tissue pad [13,86].

Finally, there are some special types of MFEs, where the film is formed *in statu nascenti* – by electrolytic reduction of a bulk modifier (intentionally admixed as a solid into the electrode material) directly during the measurements; *i.e.*, analogically to MFEs operated *in situ*. Typical examples of this kind are either a carbon paste electrode or a carbon ink (for screen-printing) modified with HgO (yellow allotropic form; [90-92]); or similar carbon paste-based substrate containing a precipitate Hg^{II} -diethyldithiocarbamate [93].

With respect to the present day's situation around mercury, there is one interesting experience which is closely associated with the task of replacing HMDEs by MFEs and which can serve as a useful inspiration in the sense of ancient Czech adage: "*Poverty taught Dalibor fiddling (the violin).*" {in original: "*Nouze naučila Dalibora housli...*" [94]}

Note: Sweden belongs among countries, where the total mercury ban has been imposed first. It had happened in the middle 1970s [4] and the respective administrative act concerned also traditional mercury drop-based electrodes, including SCE. Thus, the Swedish electrochemists and electroanalysts were factually forced to turn their attention to some alternatives; the MFE configuration having been the ultimate choice. Since then, *e.g.* Jagner's team (see [85] and refs. therein) has achieved a remarkable progress on this topic, becoming soon one of the leading groups worldwide in employing this type of electrodes in practical electroanalysis; especially, in combination with computer-controlled stripping (chrono)potentiometry and *ex-situ* operated MFEs. Their results were so unique that some members of the team had been recruited by one famous manufacturer of electrochemical instrumentation [95], collaborated then for many years, and developing as well as servicing contemporarily the only electrochemical apparatus enabling to perform analyses in the fully automated regime [96].

For many, however, the replacement of mercury drop-based electrodes with the mercury film-plated solid (substrate) electrodes seems to be rather controversial. In spite of the advantages discussed above, the most dangerous operation — from a toxicological point of view — is the deposition of mercury films from plating media, containing higher concentrations of soluble Hg^{II} salts.

Note: For example, a solution of 0.01 M HgCl_2 contains 2.7 g of this substance in 1 000 mL. And if one imagines some consequences associated with safe removal of such a waste, 10 mL of this solution must be diluted with 10 000 L of pure water (*i.e.*: 10,000,000 \times), in order to reach the levels of the highest allowable content of Hg^{II} for drinking water.

Thus, even the aspect of high toxicity of mercuric salts should be taken into account when thinking about the MFE configuration instead of HMDE.

Non-Mercury Metal-Based Electrodes as Alternative to both HMDE and MFE

With respect to the fact that this article is devoted mainly to mercury and mercury electrodes, the titled topic will be overviewed only very briefly and in basic facts. So far, this group of electrodes and the corresponding electrode materials have approached most closely the physicochemical and electrochemical properties of mercury electrodes and of the mercury itself; of course, if one omits the amalgam-based configurations.

The initial impulse came on the verge of old and new millennia, in 2000, when Wang, Hocevar et al had introduced a **bismuth film electrode (BiFE)** for modern electrochemical stripping analysis [9]. From that moment on, the BiFE together with numerous modifications and variants, has become a phenomenon of presents day's electroanalysis being the central point of interest in more than 170 scientific reports till 2009 [10] plus other *ca.* 50 contributions up until now [97]. Meanwhile, the intensive research in the newly established area of bismuth-modified electrodes spawned yet other types of non-mercury metallic electrodes based on antimony (see *e.g.* [98]; to date *ca.* 30 reports), lead ([99], 10 papers), or stannum / tin ([100], 5 contributions).

In direct confrontation with HMDE and MFEs, it can be stated that hitherto published papers on BiFEs, BiEs and all related configurations have shown that their applicability is fully comparable with respect to trace analysis of heavy metal ions, whereas their possibilities for determinations of organic pollutants, or pharmaceutically and biologically important compounds are still rather limited. This may have the reason in the incomparable surface characteristics of highly heterogeneous bismuth (crystalline) layers versus finely compact

surface of metallic mercury. However, such a comparison will be more objective as the applicability of both bismuth and mercury electrodes in organic and biological analysis will be evaluated by means of publication activities at equivalent abundance, which is now impossible as being clearly in favor of the latter, mercury-based electrodes, having been used for almost a century compared to a period of eleven years of existence of BiFEs and BiEs [10]. In this respect, only time will show...

Conclusions

In this article, we have offered a polemic around the current situation associated with the culminating aversion against mercury in all its forms and its use in modern industry and science; in our case, mainly in electrochemistry and electroanalysis. According to the surveyed facts and data, it is evident that the occurrence of mercury in the modern civilized world is very abundant and, in some fields, it will be difficult to achieve its total elimination. Surely, in selected technologies and devices, it can be replaced without problems (*e.g.* in thermometers by ethanol, in industrial production of sodium hydroxide and chlorine, in some batteries, *etc.*); nevertheless, there are special or even unique applications for which any principal restrictions or bans could be considered twice before being introduced into life. Otherwise, these activities could cause senseless and irretrievable economical losses, including consequences being almost contradictory to the original intentions.

Concerning mercury and electrochemistry, it can be concluded that the overall amount of mercury in the contemporary and typically miniaturized instrumentation seems to be reasonably low — in addition, always manipulated by well-informed personnel — to cause any serious damage to health or even life.

Thus, within the culminating efforts to impose the total mercury ban, it would be reasonable to think about any tolerance decree for some traditional and evidently useful products and laboratory devices, as a certain protection against unreasonably applied, ecologically oriented demands, as well as against all the activities responsible for the present day's hysteria around mercury — historically, one of the oldest metallic materials discovered and exploited by human population.

And nearly the same can be stated about the DME, HMDE, and MFE; all three electrode configurations deserving our continuing attention in the light of their significance in the past and countless achievements in instrumental measurements that — without them — would have never been possible.

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