SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY
SOUTH. BRAZ. J. CHEM., Vol. 7, N° 8, 1999

RECOVERY OF MERCURY FROM DENTAL AMALGAMS COLLECTED IN THE NORTHWEST REGION OF PARANA STATE, BRAZIL

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ABSTRACT

Wastes amalgams were collected from dental cabinets of northwest region of the Parana State, Brazil. Amalgams collected were washed with 0.1M nitric acid and distilled water, dried at 80^{0}C, and crushed to 100 mesh. Digestion of the brown powder were performed using two types of reactors. The first was made of pyrex glass and the second reactor of stainless steel, both connected to a PVC tube with MnO_2 and a vacuum pump. The efficiency observed was higher for the second reactor, with 96-98% of mercury recovered, and the minimum time necessary for digestion was 180 minutes. After the digestion, the mercury was transferred to a conventional apparatus for mercury distillation and purification. The distillation was performed two times and the final mercury recovered was 99% pure. Silver and tin were also recovered by chemical and electrochemical methods after the mercury separation

RESUMO

Resíduos de amálgamas dentárias foram coletados em gabinetes odontológicos na região noroeste do Estado do Paraná, Brasil. As amálgamas coletadas foram lavadas com ácido nítrico 0,1 M e água destilada, secadas a 80^{0}C e trituradas a 100 mesh. As digestões dos sólidos escuros foram realizadas em dois tipos de reatores. O primeiro reator foi construído em vidro pyrex e o segundo em aço inoxidável e, ambos foram conectados a tubos de PVC, recheados com dióxido de manganês, e então conectados a uma bomba de vácuo. O reator de aço inox mostrou maior eficiência com a recuperação de 96 a 98% do mercúrio, com o tempo mínimo necessário de 180 minutos para a digestão. Após a digestão, o mercúrio foi transferido para um aparelho convencional de destilação e purificação do mercúrio. Após a bi-destilação recuperou-se o mercúrio com 99% de pureza. A prata e o estanho também foram recuperados por métodos químicos e eletroquímicos.

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Key words: dental amalgams; mercury; environment; pollution; metal recovery

DOI: 10.48141/SBJCHEM.v7.n8.1999.79_1999.pdf

INTRODUCTION

Amalgams are mixtures of metals and mercury used to fill the teeth ,and wastes of dental amalgams consist of old amalgam, and pieces of fresh amalgam from procedures to replace deterioted fillings. Mercury (48-60%), silver (15-37%), tin (12-13%), copper (0-20%), zinc (0-1%) , and palladium (0-2%) are the average composition of dental amalgams used in dentistry. Studies performed with dental amalgams using a radioactive mercury isotope (Hg^{203}) mixed with dental amalgams fillings, and placed in the teeth of adult sheep, showed that the isotope appeared in various organs and tissues within 29 days. Evidence of mercury uptake, as determined by whole-body scanning and measurement of isotope in specific tissues, revealed three specific absorption sites: lungs, gastrointestinal tract and mandibular tissue[1]. Once absorbed, high concentrations of the isotope were found localized in the kidneys and liver.

The effect of mercury on the nervous system is a selective inhibition of protein and amino acid absorption into brain tissue. It inhibits the synaptic uptake of neurotransmitters in the brain and can produce subsequent development of Parkinson's disease. Mercury is also nephrotoxic and causes serious pathological damage[2]. Chronic exposure to mercury may cause an excess of serum proteins in the urine which may progress to nephrotic syndrome and peculiar susceptibility to infections that break into and modify the course of any pre-existing disease[3,4]. Mercury fillings can contribute to a higher level of mercury in the blood, and can affect the functioning of the heart, change the vascular response to norepinepherine and potassium chloride, and block the entry of calcium ions into cytoplasm[5]. It was also studied that mercury released from dental fillings by the practice of using chewing-gun were four times higher compared to the other patients[6]. Mercury in human body can contribute to intelligence disturbances, speech difficulties, limb deformity, and hyperkinesia (hyperactivity resulting from brain damage). Backgrounds levels of mercury in mothers correlate with incidence of fetal birth defects and still births[7].

Wastes of dense, apparently harmless, dental amalgams are usually discarded as refuse in the environment. Mercury is a heavy metal, liquid at room temperature, and with a boiling point of 358^{0}C. However, even at room temperature, the equilibrium $Hg_{(l)} = Hg_{(v)}$ exist and it slowly evaporates, emitting mercury vapor. Mercury can be converted to methyl mercury [$(CH_3)_2Hg$] by the action of anaerobic bacteria such as **Methanobacterium omelanskii**, and methyl mercury is by far the most toxic of mercury compounds. On the other hand, dental amalgams are dense solids, with high consistency and stability, and their boiling points are higher than pure inorganic mercury. Up to the present there is no clear indication about dissolution and contamination of water streams by mercury compounds released from dental amalgams. However, serious environmental problems concerned to dental amalgams are still not clear, because the temperature of furnace for cremating and solid wastes incineration could be high enough for dissolution and release of mercury vapor.

The imported mercury used in dental fillings, gold prospection, caustic soda, and chlorine production in Brazil was approximately 340 ton/year, up to 1993. Besides the amount deducted from importation, the recovery of mercury is also very important for the protection of our environment.

MATERIALS AND METHODS

Dental amalgams were collected by Dr. Jales A. Cardoso (15ª Regional de Saude de Maringa) from dental cabinets of 29 municipal districts, including Maringa County, from the northwest region of Parana State, Brazil. The amounts collected were: 30 kg (1994-1995), 40 kg (1996), and 70 kg (1997).

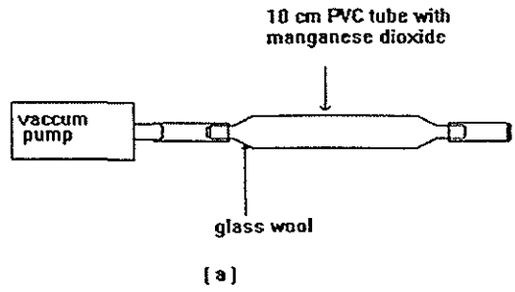
After washing with diluted nitric acid and distilled water, and drying at 80°C, the solids were crushed to a fine powder (about 100 mesh). The digestion of the brown powder was performed in two types of reactors. The first, a 500 mL pirex round-bottom flask was conected to the botton of a 250 mL pyrex erlenmeyer, and the erlenmeyer was connected to a condenser. The condenser was connected to a 1000 mL pyrex heavy-wall filtering flask, and it was connected to a 100 x 10 mm PVC tube with manganese dioxide (MnO_2 - TRONA CHEMICALS-USA), and then to a vacuum pump. As shown in a previous paper[8], manganese dioxide is an excellent material for absorption of gaseous substances including mercury, and was used to protect the vacuum pump and the environment from mercury contamination (Figure 1). The second reactor was made of stainless steel as shown in Figure 2, and a 100 x 10 mm tube of PVC with MnO_2 was also connected between vacuum pump and the filtering flask.

Powder of dental amalgams, approximately 100 g for the first and about 200 g for the second reactor, were used for each digestion. The temperature was slowly and progressively changed, and the dissolution and volatilization of Hg began at ~290-300°C. The distilled mercury collected in the filtering flask was transferred to a conventional mercury distillation apparatus for purification (Figure 6). To the collecting flask of this apparatus a 100 x 10 mm PVC tube with MnO_2 was also connected to protect the vacuum pump and the environment from contamination by mercury vapor. After the second distillation the mercury was transferred to a narrow-mouth bottle with screw cap and stored.

RESULTS AND DISCUSSION

The main disadvantage of the glass reactor was the amount used (~100 g) for digestion. Mercury liquefaction in the corner of the erlenmeyer and before the condenser was another problem observed, and solved by changing of reactor design, as shown in Figure 1. The residue left after digestion and mercury separation was constituted by the oxides of tin, silver,copper, etc. Mercury determination in this residue by cold vapor atomic absorption spectrometry was an important step to calculate the efficiency of mercury separation and recovery. The average efficiency observed was 95% for the glass reactor and 96-98% using the stainless steel reactor. The mercury released as vapor and absorbed on MnO_2 was also determined by cold vapor atomic absorption spectrometry.

Figure 2 shows the stainless steel reactor. The main disadvantage was the superficial corrosion observed after several hours of heating. With 200 g of brown powder inside the reactor, the temperature was slowly increased and the dissolution and volatilization of mercury began at 290-300°C using the PVC tube with MnO_2 and a vacuum pump. Without the vacuum pump and the PVC tube with MnO_2, the minimum temperature for digestion and volatilization of mercury was > 500°C. Figure 3 shows the efficiency of mercury recovered as function of heating time using stainless steel reactor. The amount of manganese dioxide used inside the PVC tube is very important. Higher amounts of manganese dioxide required higher temperature for mercury volatilization as shown in Figure 4, and 25-30g of manganese dioxide should be used and



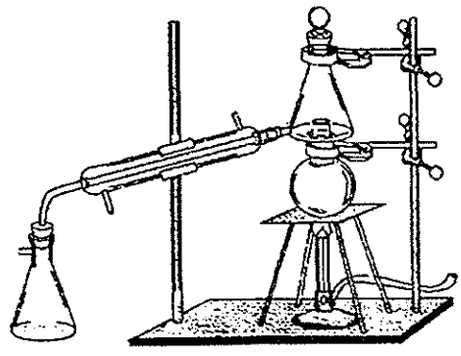


Figure 1. Glass reactor used for amalgams digestion. A 500 mL pirex round-bottom flask, with ~100g of amalgam powder (100 mesh), was used as reactor.[a] 10cm PVC tube with manganese dioxide and glass wool was connected between the vacuum pump and an erlenmeyer collecting flask.

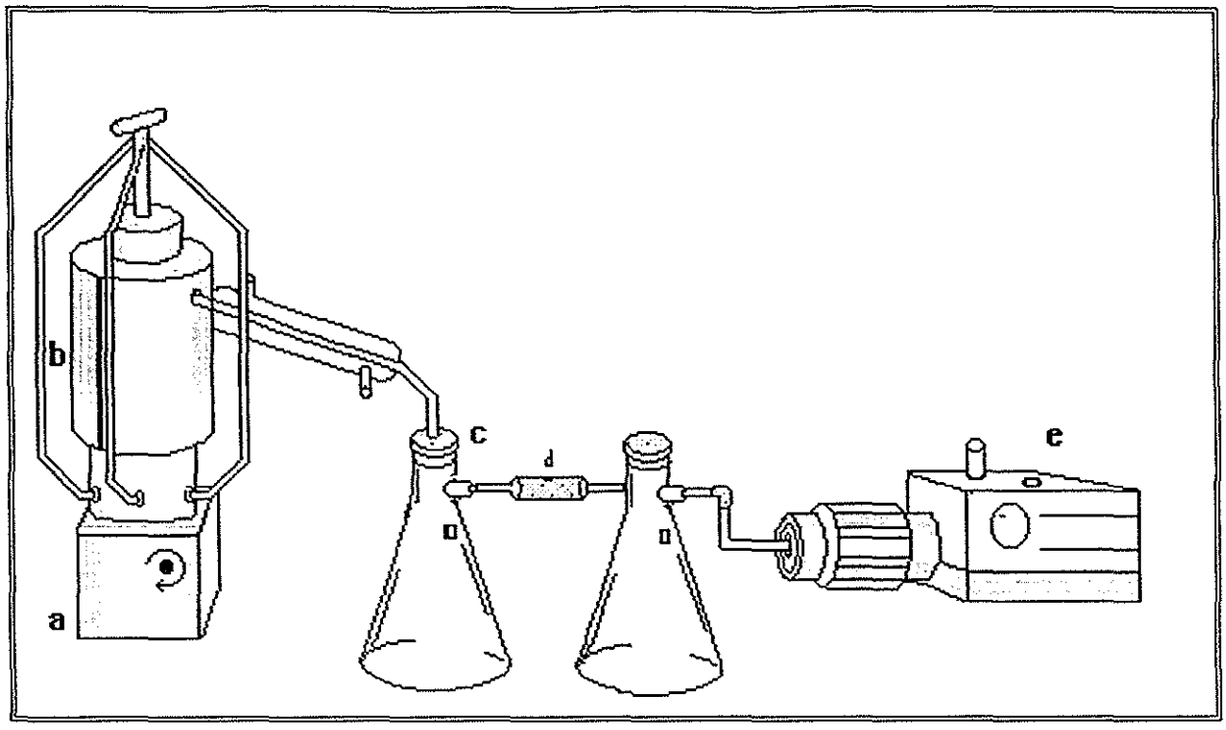


Figure 2. Stainless steel reactor used for amalgams digestion. A 10cm PVC tube with manganese dioxide and glass wool was also connected between the collecting flask and vacuum pump.
a) Rheostat. b) Stainless steel reactor. c) Collecting flask. d) PVC tube (10 x 100 mm) with MnO_2 . e) Vacuum pump.

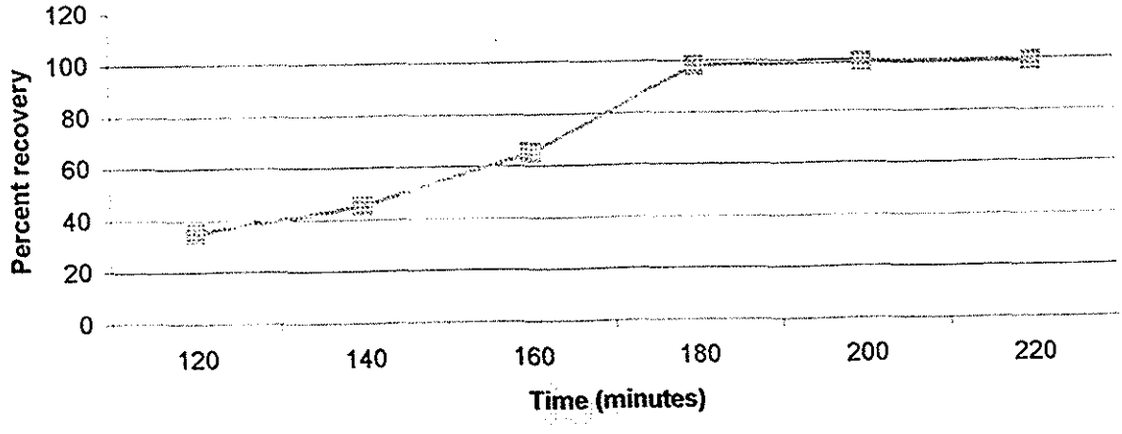


Figure 3. Percent recovery of mercury as function of heating time using a stainless steel reactor. The digestion temperature using the vacuum pump was 295 ± 10^{0}C, and the amount of amalgam powder used was 200g. The digestion temperature using the vacuum pump was 295 ± 10^{0}C, and the amount of amalgam powder used were 200 g.

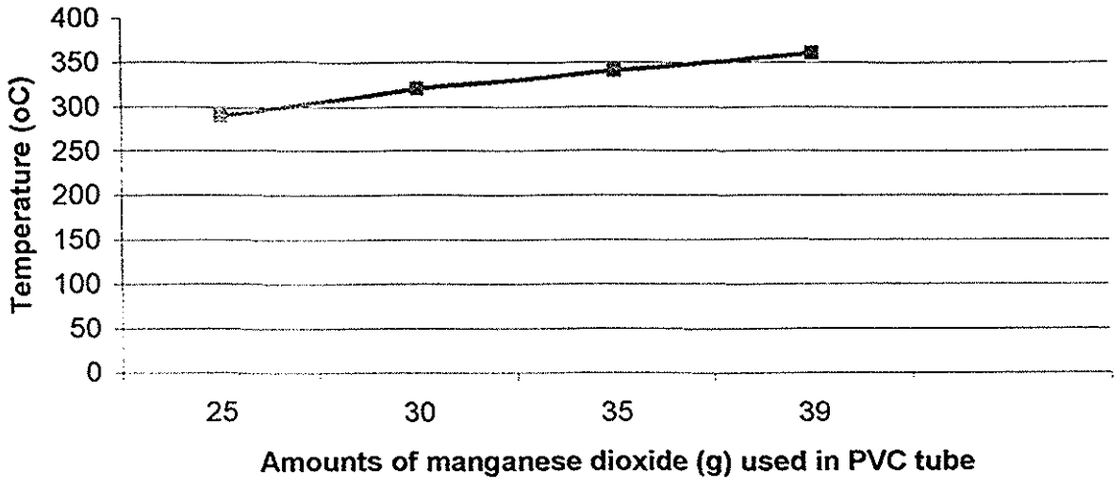


Figure 4. Dependence of Hg volatilization from dental amalgams as function of amount(g) of manganese dioxide used inside the PVC tube. The experiment was performed using a stainless steel reactor with ~200g of dental amalgam powder.

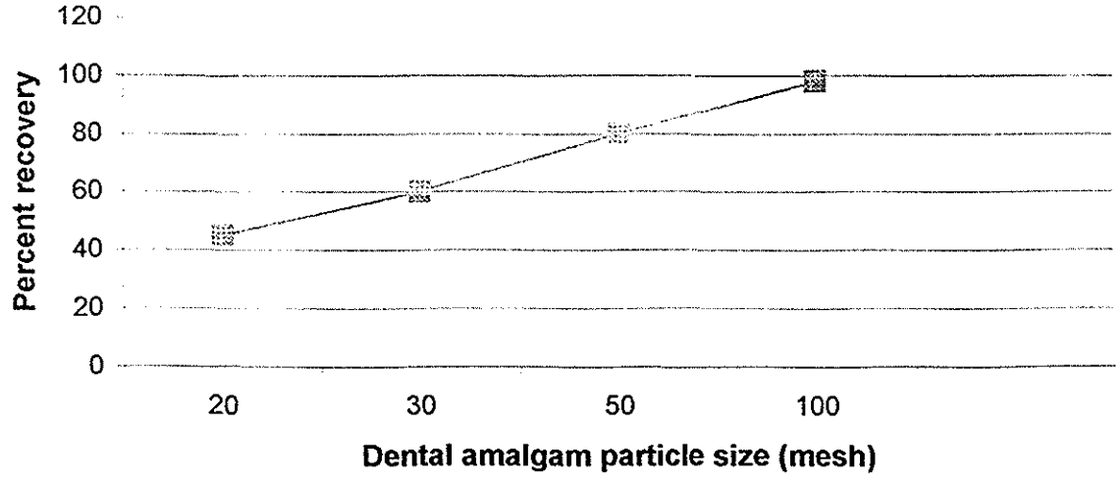


Figure 5. Recovery efficiency (%) of mercury as function of dental amalgam particle size (mesh). The experiment was carried out using a stainless steel reactor with ~200g of dental amalgams, and 25g of manganese dioxide inside the PVC tube.

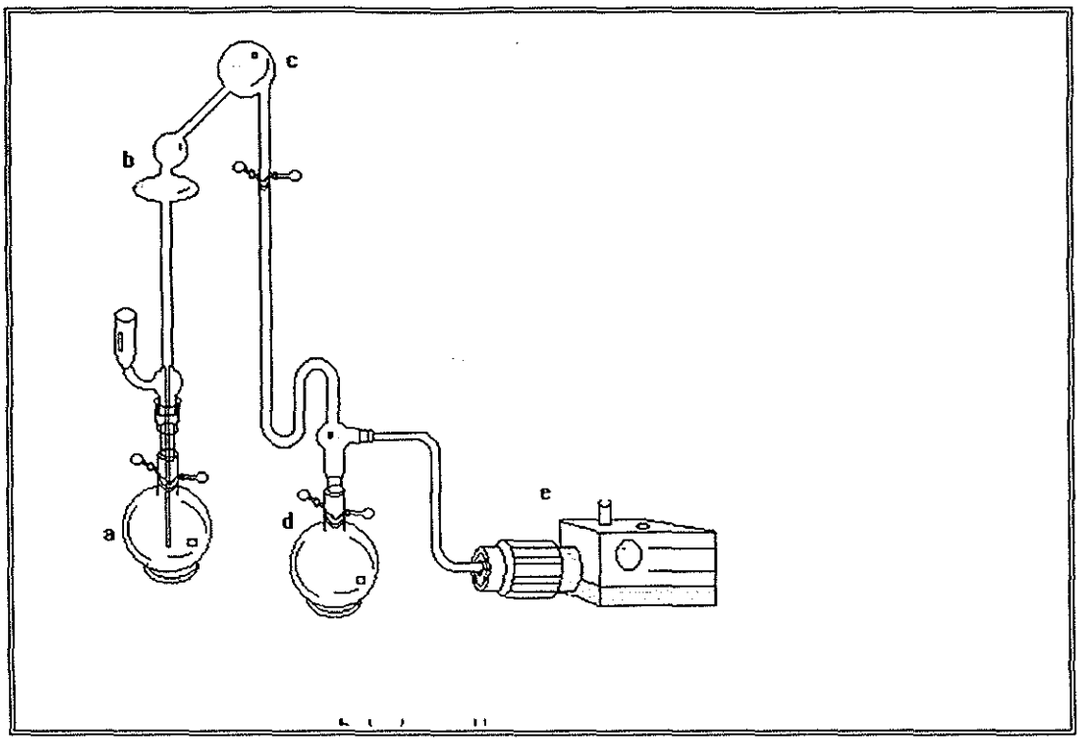


Figure 6. Apparatus used for final mercury purification after separation of silver, tin, copper, zinc, etc., from dental amalgams.[a] Flask with mercury to be purified. [b] Heating device. [c] Condenser. [d] Collecting flask.[e] Vacuum pump. A 10cm PVC tube with manganse dioxide and glass wool, not shown in the figure, was also connected between the collecting flask and vacuum pump.

changed after 24 hours of continuous operation. Amalgam particles size are also important, and higher efficiency was observed with smaller particles size of dental amalgams, as shown in Figure 5.

The environmental problem by mercury released from wastes of dental amalgams could be solved using one of the reactors investigated. Recovery efficiency was very high and the main advantage were low cost, simple operation, and high purity of the mercury recovered. The PVC

tube with MnO_2 connected between the collecting flask and vacuum pump was very important for the absorption of mercury vapor, that otherwise could cause problems to the vacuum pump and the environment. However, the amount of MnO_2 should be carefully investigated, because, with high amounts of MnO_2 the efficiency of the vacuum pump will be lower. The digestion temperature of amalgams was 290-300^{0}C using PVC tube with MnO_2 and vacuum pump, and at least 500^{0}C without the vacuum pump.

ACKNOWLEDGEMENT

The authors would like to thank National Foundation of Environment (FNMA-Brazil), Brazilian Council of Scientific and Technological Development (CNPq, CNPq/PIBIC-Brazil) for fellowships and financial support, and Dr. Jales A. Cardoso (15ª Regional de Saude de Maringa-PR.) for supplying the amalgam samples.

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