

## Exposure to mercury vapor from dental amalgam estimated with Zeeman atomic absorption spectroscopy.

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**Abstract:** Previous methods for the determination of intraoral mercury vapor ( $\text{Hg}^\circ$ ) release used principally some form of preconcentration of Hg on gold, allowing relatively few measurements with unknown precision and sensitivity at selected times. Recently available computer-controlled Hg detectors operating on Zeeman atomic absorption spectroscopy (ZAAS) facilitate the direct real-time measurement of  $\text{Hg}^\circ$  concentrations. It was the aim to adapt this method for a comparative investigation of emission processes from fillings in situ and from amalgam specimens in-vitro. An electronically controlled sampling protocol integrated the instrument operation, the coordination of air flows and the data collection. The rate of  $\text{Hg}^\circ$  emission was not affected by a 7-fold change of the flow rate of sampling air. After stimulation of amalgam specimens and of fillings in-situ, the emission decayed exponentially (halftimes 8.6 and 10.7 min). Precision was evaluated by a series of measurements on a single patient which indicated a consistently low coefficient of variation between 18 % and 25 %. After insertion of a few new fillings, sensitivity was high enough to detect a significant increase in resting emission over that from the majority of old fillings. Conclusion: Zeeman-AAS in connection with semi-automated sampling and data storage provides precise in-situ measurements of  $\text{Hg}^\circ$  emission from dental amalgam with real-time resolution.

**Key words:** amalgam, mercury vapor, mercury emission, oral air, Zeeman atomic absorption spectroscopy

### Introduction

Long-term exposure of the general population to mercury vapor ( $\text{Hg}^\circ$ ) occurs mainly from the release of small amounts of  $\text{Hg}^\circ$  from dental amalgam fillings<sup>[1]</sup>. An assessment of the possible health risks arising from this release is based on the accurate estimation of the exposure dose to mercury which is reflected mainly by the emission of  $\text{Hg}^\circ$  from the fillings. When an open flow-through system is used the concentration of  $\text{Hg}^\circ$  in oral air depends on the emission rate by the relation<sup>[2]</sup>:

$$\text{concentration (ng/L)} = \text{emission (ng/min)} / \text{flow (L/min)} ; (\text{eq. 1})$$

Gold-film analyzers and techniques of precollection on silver or gold wool used so far for this purpose lack flexibility because of fixed aspiration times, pump rates and Hg desorption from the gold after a number of measurements. Due to the dilution with Hg-free outside air during sampling (eq. 1), the concentration of  $\text{Hg}^\circ$  in the cell of conventional atomic-absorption spectrometers (AAS) is too low to provide reliable data. The recent introduction of the Zeeman principle in portable AAS monitors with an

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optical length of nearly 10 m lowered the detection limit to the pg/L range in connection with a continuous data acquisition at high-rates. It was the objective, therefore, (1) to verify the appropriate conditions according to eq. (1) in experiments with isolated amalgam specimens, (2) to evaluate the precision and sensitivity of this method by a series of measurements on the same patient before and after a small change in amalgam status, and (3) to take advantage of the improved analytical performance for a detailed exploration of the release kinetics of Hg vapor. Aim (2) has never been examined for any procedure of measuring intraoral Hg<sup>0</sup> release.

## Method

The measurements were performed with a portable Hg-vapor detector with Zeeman AAS (Hg-analyzer RA-915; Lumex, St. Petersburg, Russia), using the software of the manufacturer installed on a notebook computer. Sample air was drawn with an external membrane pump placed downstream of the instrument (Fig. 1). The air flow was regulated by a mass flow controller inserted between the pump and the instrument. When the Hg<sup>0</sup> emission from amalgam pellets was investigated the instrument was operated in the continuous mode for 60 min. Intraoral concentration data were recorded in an automated sampling protocol activated by a programmable time-switch controller. The sampling cycle started with the removal of residual Hg<sup>0</sup> from the mouth with pressurized air and the simultaneous aspiration of room air into the Hg-analyzer before oral air was drawn for 60 sec of which the last 30 sec were recorded as concentration signal (average from 30 data points). The cycle terminated with a 30-sec reference recording of room air (Fig. 3). Each cycle was preceded by two rinses of the mouth with water. A 37-year old woman from the institute's staff, who had 9 old amalgam fillings with a total of 16 surfaces, volunteered for the measurements. During the course of the investigation, she had inserted new amalgam fillings solely on her own decision.

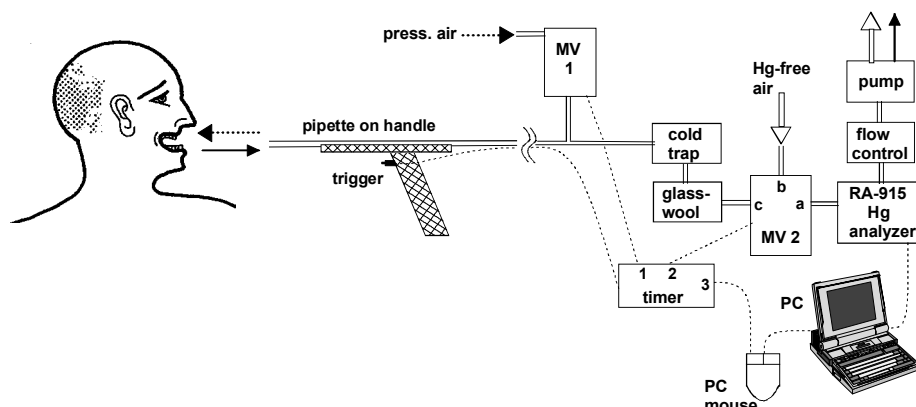


Fig. 1: Components of the system as used for measurements of oral air. The cold trap consisted of two impingers in series submersed in crushed ice. MV: magnetic valves. Dotted lines: electrical connections. Arrows: dotted: pressurized air; solid: oral air; empty: room air.

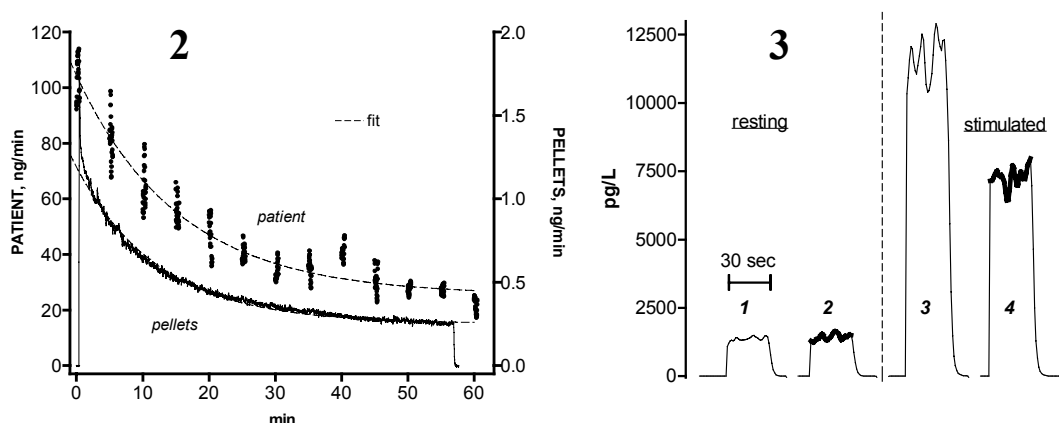
## Results and Discussion

### *Measurements on amalgam pellets*

Upon the slightest manipulation of amalgam pellets, a high initial emission rate was noted which declined exponentially to a near steady state after 1 hour, following the equation:

$E = 0.939 \text{ ng/min} \times e^{-0.08058 \times t} + 0.252 \text{ ng/min}$ ; ( $R^2 = 0.9759$ ; 3400 points; decay half-time 8.6 min; Fig. 2). Thus, after a waiting time of 1 hour the relation of eq. 1 could be

tested. While the air flow was increased from 0.7 to 4.8 L/min, the emission varied only between 0.3 and 0.33 ng/min, confirming that the concentration measurements were in accordance with eq. 1 (data not shown).



**Fig. 2:** Decay of  $\text{Hg}^\circ$  emission rate from stimulated amalgam pellets and from fillings in situ. **Fig. 3:** Original recording of one daily run of four concentration measurements of  $\text{Hg}^\circ$  in oral air (before and after stimulation). *Italics: number of measurement as in Tab..* For clarification, the 30 data points representing the average of a particular concentration value are shown as bold trace in measurements 2 and 4.

#### *Intraoral measurements*

Reproducibility was tested at unchanged amalgam status in 14 measurement sessions (daily runs) over 22 days. A daily run consisted of duplicate measurements before (nr. 1 and 2, resting amalgam) and after chewing gum for 10 min (nr. 3 and 4, stimulated amalgam; Fig. 3). Standard deviations increased with increasing mean values of the four groups of 14 identical measurements, indicating little change in the coefficients of variation (between 18 and 25 %; Tab.) and a consistent precision over the entire working range. While measurements 2 turned out to duplicate measurements 1, measurements 4 were significantly lower than measurements 3 (Tab.). No outliers had been identified by the Grubb's test in the 4 groups of measurements<sup>[3]</sup>. 5 days after finishing the series of 14 daily runs, the patient underwent dental therapy which left her with 14 old and 4 new surfaces of 8 old and 3 new amalgam fillings respectively. 6 runs at days 1, 2, 3, 77, 78, 79 after this treatment showed consistently elevated values in each group of measurements (Tab.). It can also be seen that the precision of the measurements rendered the method so sensitive that a small increase in resting emission by only 6 ng/min was detected at a very low level of significance. To study the decay of emission, automated measurements were taken every 5 minutes for one hour immediately after stimulation (each measurement preceded by one rinse with water). As with amalgam pellets, the resulting emission rates declined exponentially according to the equation  $E = 79.0 \text{ ng/min} \times e^{-0.06464 \times t} + 25.40 \text{ ng/min}$ ; ( $R^2 = 0.9381$ ; 390 points; decay halftime 10.7 min; Fig. 2). This explains the consistent difference between the first two measurements after stimulation (Fig. 3; Tab.) which were separated by an interval of a few minutes.

The new method permitted the kinetic analysis of the emission from stimulated amalgam

specimens, which revealed a perfect fit of the data to a half-time model (Fig. 2). The exponential decay of the emission may be explained by the incremental buildup of layers that each reduce the momentaneous  $\text{Hg}^0$  release. Alternatively, microdroplets of  $\text{Hg}$  could be formed at freshly stimulated amalgam surfaces<sup>[4]</sup>. In this case,  $\text{Hg}^0$  would evaporate from a steadily decreasing surface area of the droplets and again produce a first-order decay of  $\text{Hg}^0$  emission. Thus, the initial phase of high  $\text{Hg}$  release may gradually subside with the completion of new surface films or with the evaporation of the microdroplets, leaving a low basal emission rate across intact surface layers. The similar decay kinetic of the stimulated intraoral emission seemed to indicate a mechanism common to amalgam in-vitro and in-situ. The similar quality criteria of the fits for the in-vitro and intraoral emission-decay curves also demonstrate the high reproducibility of the intraoral measurements, which would not have been the case if the intraoral procedure was prone to random error.

group of measurements	old fillings (n = 14)				old + new fillings (n = 6)			
	resting		stimulated		resting		stimulated	
	1	2	3	4	1	2	3	4
mean (ng/min)	11.4 <sup>a</sup>	11.5 <sup>b</sup>	95.5 <sup>c, e</sup>	60.4 <sup>d, e</sup>	17.3 <sup>a</sup>	17.3 <sup>b</sup>	157.9 <sup>c, f</sup>	85.9 <sup>d, f</sup>
SD	2.3	2.9	17.1	13.2	3.9	3.1	20.9	10.7
var. coeff. (%)	19.7	25.1	17.9	21.9	22.5	17.9	13.2	12.5
median	11.8	12.4	101.3	63.9	16.2	17.1	157.6	90.8
95% c.i., lower	10.3	10.0	86.5	53.5	14.2	14.8	141.2	77.3
95% c.i., upper	12.6	13.0	104.5	67.3	20.5	19.8	174.6	94.5

two-sided t-tests: <sup>a</sup>) - <sup>d</sup>)  $p < 0.001$ ; <sup>e</sup>), <sup>f</sup>)  $p < 0.0001$

**Tab.:** Summary of 14 daily runs of emission measurements (ng/min) taken on one patient over a period of 22 days, and of 6 daily runs taken during 79 days following the insertion of three new amalgam fillings. *Italics: numbers of measurements as in Fig. 3.*

## Conclusion

Direct concentration measurements with Zeeman AAS in connection with a programmed sampling protocol facilitate a precise observation of rapid and slow  $\text{Hg}^0$ -emission processes from amalgam specimens as well as from fillings in situ. Considering this versatility, the method should be useful in studies with many participants.

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