



Round Robin Test *Report*

Mercury Determination in Fluorescent Lamps

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1. Introduction

Mercury in fluorescent lamps

Fluorescent, both straight (FL) and compact fluorescent lamps (CFL) cannot work properly and reach high energy efficiency without a small amount of mercury. A low pressure mercury discharge is established inside the lamp, which generates UV radiation. The UV is subsequently transformed into desired visible light by the fluorescent powder layer on the inner lamp surface. This amount of mercury must be accurately dosed in the lamp during the manufacturing process. Various dosing technologies exist to add the mercury to the lamp.

Mercury content needs to be known

Legal developments make it imperative that the amount of mercury is precisely known and that it does not exceed the set limits.

Since 2006, fluorescent lamps for general lighting have to satisfy limits set by the EU Directive on Restriction of Hazardous Substances (RoHS) (ref 1A)¹. For CFL lamps the current limit is 5 mg, and for FL lamps limit values are either 5 , 8 or 10 mg depending on phosphor coating material composition (halophosphate or tri-band phosphor) and life time requirement (long life lamps may have more mercury). Currently, the exemption list is under formal review, and based on the assessment of scientific and technical progress, much lower limit values are to be expected in the revised list, which is due for publication in 2010. A second major requirement is that, as of 13 April 2010, the mercury content has to be published. This information requirement is part of a so-called Implementation measure of the Energy Using Products Directive (ref 1B)².

¹ Directive 2002/95/EC on the Restriction of the use of certain Hazardous Substances in Electrical and Electronic Equipment (RoHS)

² COMMISSION REGULATION (EC) No 245/2009 implementing Directive 2005/32/EC of the European Parliament and of the Council with regard to ecodesign requirements for fluorescent lamps etc. (requires labeling as X.X mg)

Standard development

For determination of material content of the six RoHS substances, an IEC standard 62321 has been established (ref 1C)³. However, for the particular case of mercury in lamps, is not considered by the Lighting Industry as suitable for a common and reliable evaluation of the mercury contents in lamps. For this purpose IEC SC 34A is developing a specific test method in prIEC 62554 (ref 1D)⁴

Guidance on market surveillance

Ahead of this latter standard development, ELC has provided an initial guidance for market surveillance on mercury in fluorescent lamps in 2007 (ref 1E)⁵. The ELC intends to update its guidance based on the new standard and on round robin results.

Participants

The following laboratories have participated in this Round Robin FL test (in alphabetical order)

1. GE Hungary
2. Hitachi co. Ltd
3. Nippon Instruments Corporation
4. NLTC Beijing
5. Osram Europe
6. Osram Sylvania
7. Panasonic co. Ltd
8. Philips Research MiPlaza
9. Philips Lighting Shanghai, China
10. Toshiba Lighting & Technology co. Ltd
11. VDE
12. WESSLING Bochem

³ IEC 62321 Ed.1: Electrotechnical products - Determination of levels of six regulated substances (lead, mercury, cadmium, hexavalent chromium, polybrominated diphenyls, polybrominated diphenyl ethers)

⁴ prIEC 62554 Ed.1: Measurement of mercury level in fluorescent lamps (CD status)

⁵ The ELC Guidance Document on Market Surveillance for the RoHS Directive (2002/95/EC), 28 June 2007, www.elcfed.org

2. Round Robin Test setup

Principle

A Round Robin test is a test (measurement, analysis) performed independently several times. This can involve multiple independent laboratories performing the test with the use of the same method in different equipment, or a variety of methods and equipment. In reality it is often a combination of the two.

The main reason for performing a Round Robin test is a verification of a method of analysis: If a method of analysis has been developed, a Round Robin test involving proven methods would verify whether the new method produces results that agree with the established method. All types of Interlaboratory tests are referred to as "round robins". Round Robin occurs in the specific case of all participants actually evaluating or testing the exact same test object.

Test samples are prepared under controlled conditions with precise dosing. Mercury measurement requires destructive testing. Preparing the analyses requires a level of accuracy so the results give detailed information on the original dosing. The purpose of the round robin is to establish that the participating laboratories are not only good on paper but do carry out testing well enough to meet the required standard.

This forms the basis for next Round Robin fluorescent lamp tests.

Round Robin FL testing

The Round Robin fluorescent lamp test is needed because different laboratories use multiple testing methods, which do not necessarily provide a fair standard of judgment in case of law violation.

The main categories of fluorescent lamps are straight fluorescent lamps (FL) and compact fluorescent lamps (CFL). For the first round robin, FL lamp type has been selected, due to its relatively simple and highly standardized shape (so-called 4ft T8 lamp).

The Round Robin FL testing is for Interlaboratory comparisons to determine the performance of individual laboratories for specific test and to monitor laboratories' continuing performance. Participation in Round Robin FL testing schemes provides laboratories with an objective means of assessing and demonstrating the reliability of the data they are producing. So, the Round Robin FL tests allow laboratories to check their normal, routine performance and to compare their results with those of other laboratories.

Subsequently in the follow up of the Round Robin FL test the laboratories have the chance to upgrade their performance by learning from other laboratories and refine their protocols.

A third Round Robin FL test can be executed to fine-tune the protocols and describe a worldwide uniform protocol to perform the mercury analysis in fluorescent lamps. Also CFL lamps can be included in next Round Robins.

Laboratories participating in the world-wide laboratory Round Robin program, receive valuable information about the technical capability of its laboratory. This provides the lab (personnel, QA-manager and the management) and also its (potential) clients a good indication of its analytical competence. The responsible management can use the results and conclusions to diagnose and cure causes of deviating results if present. The program can be incorporated in the quality assurance systems of the laboratory to gain maximum profit. The performance of a laboratory participating in the Round Robin FL test may be taken into account by the European Lamp Companies Federation (ELC) with confidence.

Using strict protocols, the participating laboratories all analyze the same samples in the same period. Each laboratory uses routine procedures, generally validated standard methods (either reference method or alternative methods IEC 6251), which are used in day-to-day practice. The results are collected by Philips Lighting. Equipped with standard tools and independently statistically processed by CQM (Consultants in Quantitative Methods).

The Fluorescent lamps are all produced in one production run in the Philips Lighting factory in Roosendaal. The mercury is dosed in the lamps in glass pills which are opened after closing the fluorescent lamp. Accordingly no mercury losses occur during the lamp making process. The mercury pills are specially made, to avoid big spreads and outliers in the mercury content. Consequently, the Hg spread is very low.

Each laboratory will receive a certain number of lamps and a certain number of pills. These numbers of lamps and pills is constraint by practical considerations and is expected to amount to five each. It will be assumed that the uncertainty about the actual content of Hg as measured by the Philips factory in Roosendaal is very small compared to the measurement variation shown by the different laboratories. Since all measurements are destructive lamps fabricated close together in time will be seen as multiple births. We could call them pseudo replications. In this way each laboratory delivers multiple measurements obtained from the 'same' object. From these measurements a point estimate and a 95%-confidence interval for the mean and the standard deviation will be generated. Testing whether means and standard deviations differ between laboratories is a logical next step. Results will be reported by organizing Laboratory.

Setup

1. Philips Lighting factory Roosendaal (The Netherlands) have produced lamps and pills;
2. Lamps and pills were partly tested at Philips Research Miplaza to gather spread information;
3. Two series of 5 lamps (with different dosed amounts of mercury) and two series of 5 glass pills (with different dosed amounts of mercury) were sent to all participants;
4. Each testing lab analyzed the amount of Hg in all lamps and pills according to their preferred method;
5. Each testing lab sent back their results to TMA Miplaza. TMA Miplaza provided CQM all the results to be statistically processed;
6. TMA Miplaza collected the results in this report;

3. Way of Working

The total mass of mercury per lamp, measured in mg, needs to be determined. XFR techniques are not applicable, detailed wet-chemical material analysis shall be applied instead. Best techniques are Cold-Vapour Atomic Absorption Spectroscopy (CV-AAS) and Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES). Sample preparation and analytical determination of mercury content in a lamp needs specific attention to yield reliable measurement values. Depending on production process mercury content in compact and straight fluorescent lamps can vary from lamp to lamp.

For mercury content measurement standard IEC 62321 Ed1 /CDV; "Determination of Mercury in Polymers, Metals and Electronics by CV-AAS, AFS, ICP-AES, and ICP-MS" has to be applied in order to get comparable measurements.

During sample preparation it has to be made sure, that mercury does not get lost due to evaporation. Unfortunately sample preparation according to IEC 62321 Ed1 is not suitable for compact and straight fluorescent lamps. One of the sample preparation methods that are specified in CDV of IEC62554 standard (draft) have to be used in order to get reliable results instead.

Sample preparation may be dependent in which way mercury is dosed into the lamp (example: dosed as fluid substance or in a solid amalgam material).

CFL/FL	Hg
Product sampling	Sample size: 5+5
Sample preparation	Test lab preferred method(s) of CDV of IEC 62554
Material analysis	IEC 62321 Ed1 Wet chemical analysis: CV-AAS ; ICP-AES
Data analysis	Hg as mg/lamp

Table 1 Process steps for typical fluorescent lamps

There is a wide variety of mercury dosing solutions including appearance and placement of mercury dispensing devices and also composition and structure of those devices. Although some of the lamps are dosed with amalgam or solid mercury alloy, there are also many fluorescent lamps dosed with liquid mercury.

Sample Preparation

Each laboratory is asked to use its own method for determining the amount of Hg in the lamps. However, the IEC document 62554/CDV is a tool for a general method development of this analysis.

The detailed procedure is described in 62554/CDV (IEC): “SAMPLE PREPARATION FOR MEASUREMENT OF MERCURY LEVEL IN FLUORESCENT LAMPS”

For the purposes of the present document, the same terms and definitions apply as described in IEC document 62554/CDV.

A small overview of these techniques as mentioned in 62554/CDV is described below:

Cold Spot Method:

Cold spotting is a method for condensing free mercury in a localized position. The cold spotting method minimizes the loss of mercury in vapour phase when the arc tube is opened. As cold spotting collects mercury from any part of the lamp into a small cold surface it allows a superior control on mercury recovery for the measurement.

The mercury localization occurs while the low-pressure discharge lamp is “ON” under normal operating conditions while a small area (the cold spot) of the discharge tube is maintained at a low temperature. During the mercury collection the lamp shall be normally operated with properly selected control gear.

When the free mercury is fully collected, the light output of the lamp will drop significantly and the discharge colour will typically turn “pink”. The process of collecting the free mercury to the cold spot is then completed. The collection time depends strongly on the amount of available free mercury.

Sample containers shall be as follows:

- Use 250 ml or 500 ml wide mouth screw-capped plastic bottle for cold spot section as first container;
- Use 125 ml wide mouth screw-capped plastic bottle for end portions of discharge tube as second container;
- Use 250 ml, 500 ml, 1 000 ml or 2 000 ml wide mouth screw-capped plastic bottle for glass parts of discharge tube, depending on which one fits better to the discharge tube dimensions under test as third container.

The sample preparation shall be executed according to the below listed process steps

- Separate discharge tube from its fragment retention cover, if any.
- Mark discharge tube in a non-destructive manner for first sectioning. Mark 12 cm from the labelled end for the initial cut; mark 6 cm on both sides of the cold spot.
- Collect the free mercury with cold spotting until mercury starvation is verified.
- Remove lamp from cooler. Keep lamp horizontal until sectioning.
- Place the lamp on cutting table covered by bench coat – with the plastic side up, toward the lamp.
- Score and break the discharge tube at the first mark allowing the arc tube to fill with air slowly so that no fluorescent powder coating of the tube is blown off.

-Score and break the lamp at the remaining two marks. Place cold spot section (12 cm) immediately into the first container. Close the first container. Shake the first container allowing the discharge tube section to crush. Keep the first container in crushed ice until digestion. Allow 5 min for the floating dust to settle before continuing. Proceed to the sample digestion immediately.

Next, separate discharge tube from its plastic and metallic surrounds. Cut associated lead wires as close to the glass seal as possible. Only the discharge tube will be used for mercury level measurement.

Score both of the lead wire containing ends of the discharge tube approximately 7 mm from the end of the tube. Pre-score discharge tube for sectioning. Use the minimum possible number of sections allowing the parts to fit into the third container.

Section the ends of the discharge tube using hot rod or wire at scores marked. Score and break tip offs and check for metal parts. Crush tip offs with pliers into the second container. Check end portions for any hollow glass objects and crush them gently with pliers into the second container. Carefully avoid touching the content of hollow glass objects with the pliers. Place the end portions – inclusive of metal parts in them – of the discharge tube into the second container and close the second container.

Section the remaining discharge tube using hot rod or wire at scores marked in step 0.

Place discharge tube sections into the third container.

Check bench coat for material chips. Any material on bench coat shall be placed into the third container. Then close the third container.

Shake the third container allowing the discharge tube to crush. Allow 5 min for the floating dust to settle before opening. Samples are ready for digestion.

The glass sample digestion shall be executed according to the below listed process steps

-Add 25 ml concentrated nitric acid. Add 10 ml water and swirl to mix.

-Add 0,25 ml of 5 % potassium permanganate and allow to stand for 16 h (overnight) in a well-ventilated fume cupboard.

The metal sample digestion shall be executed according to the below listed process steps

-Add 3 ml concentrated hydrochloric acid and 1 ml concentrated nitric acid.

-If dissolution is incomplete, add 2 ml HF in 2 ml increments. When all metals are dissolved, add 20 ml nitric acid. Add 10 ml water and swirl to mix.

-Add 0,25 ml of 5 % potassium permanganate and let stand for 16 h (overnight) in a well-ventilated fume cupboard. [ref: 3A]

Nitric acid rinse method

Sample containers shall be as follows:

-Use 125 ml plastic sample beaker for end portions of discharge tube as first container;

-Use 250 ml plastic sample beaker as second container.

The sample preparation shall be executed according to the below listed process steps

- Separate discharge tube from its fragment retention cover, if any.
- Separate discharge tube from its plastic and metallic surrounds. Cut associated lead wires as close to the glass seal as possible. Only the discharge tube will be used for mercury level measurement.
- Carefully break the tip-off, crush and collect it into the first container. Inject a volume of concentrated nitric acid 1/30th of the lamps interior volume using a Pipette having no attached needle.
- Holding the lamp in a near horizontal orientation, rotate the lamp such that the acid contacts all interior surfaces. Place the lamp in a vertical orientation for 15 min. Repeat this procedure a minimum of three times.
- Remove the open tip-off end of the lamp (approximately 2 cm) using a diamond pen or hot wire and place the 2 cm section including the coil mount into the first container. Decant the concentrated nitric acid from the lamp into the second container.
- Wash the interior of the lamp with water and decant into the second container. Wash the interior of the lamp a minimum of five times.

- Remove the other end of the lamp (approximately 2 cm) using a diamond pen or hot wire. Crush tip off with pliers into the first container and place the 2 cm section including the coil mount into the first container.
- Add an appropriate volume of concentrated nitric acid and stay for more than 15 min.
- Decant the concentrated nitric acid from the first container into the second container and wash the first container a minimum of three times with water and decant into the second container.
- Remove all glass components from first container and leave only metallic components.

The glass sample digestion shall be executed according to the below listed process steps

- Add 25 ml concentrated nitric acid. Add 10 ml water and swirl to mix.
- Add 0,25 ml of 5 % potassium permanganate and allow to stand for 16 h (overnight) in a well-ventilated fume cupboard.

The metal sample digestion shall be executed according to the below listed process steps

- Add 3 ml concentrated hydrochloric acid and 1 ml concentrated nitric acid.
- If dissolution is incomplete, add 2 ml HF in 2 ml increments. When all metals are dissolved, add 20 ml nitric acid. Add 10 ml water and swirl to mix.
- Add 0,25 ml of 5 % potassium permanganate and let stand for 16 h (overnight) in a well-ventilated fume cupboard. [ref: 3A]

Methods to determine the amount of Hg in fluorescent lamps

Each laboratory was free to choose its analyzing technique. Below is a short description of the used techniques:

Cold Vapour Atomic Absorption Spectrometry (CV-AAS)

Cold vapour AAS is used for the determination of low amounts of mercury. The sample solution is mixed with a strong reducing agent (for example SnCl_2). The atomic mercury that is formed is transported as a vapour out of the solution by an Ar flow. The Ar flow is transported into a quartz cuvet that is placed in a light beam. In the cuvet the actual measurement is performed via absorption of light by the atomic Hg (253.7nm).

Inductively Coupled Plasma- Atomic Emission Spectrometry (ICP-AES)

ICP-AES is a technique for elemental analysis. Its high specificity, multi-element capability and good detection limits result in the use of a large variety of applications. All kinds of dissolved samples can be analyzed, varying from solutions containing high concentrations to diluted acids.

In this perspective, ICP-AES can be used for the Hg determination in fluorescent lamps. Specific wavelengths (preferred 194.168 nm) are used.

A plasma source is used to excite atoms to a higher energy level. They return to their ground state by emitting photons of a characteristic wavelengths. This light is recorded by an optical spectrometer. When calibrated against standards the technique provides a quantitative analysis of the original sample.

4. Preparation of the Hg pills

The Round Robin on Hg testing in fluorescent lamps is about determining the accuracy of different laboratories in how each laboratory determines the total amount of Hg in a new fluorescent lamp (zero hour burnt). In this way, it is very important to produce fluorescent lamps with a spread in dose weight of Hg as small as possible. This chapter shortly follows the procedure on how the mercury is dosed in separate Hg pills to ensure an accurate known amount of Hg. For reference, the Hg pills are tested via cold vapour AAS to know the regular error and variance between all Hg pills.

Dosing and sealing the Hg pills

The dosing procedure starts when indexing all glass (half open) capsules wait in line in the machine:

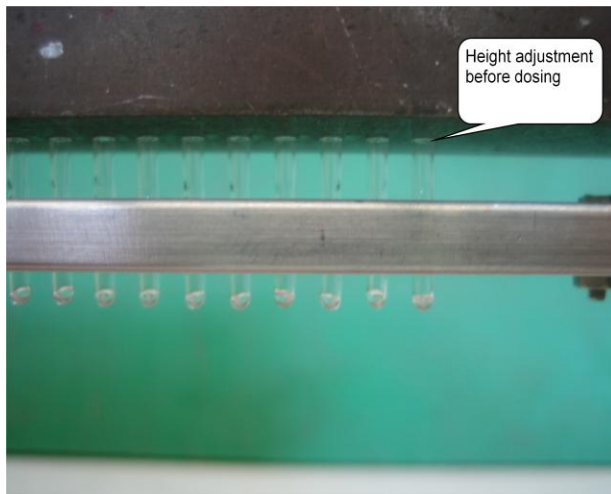


Figure 1

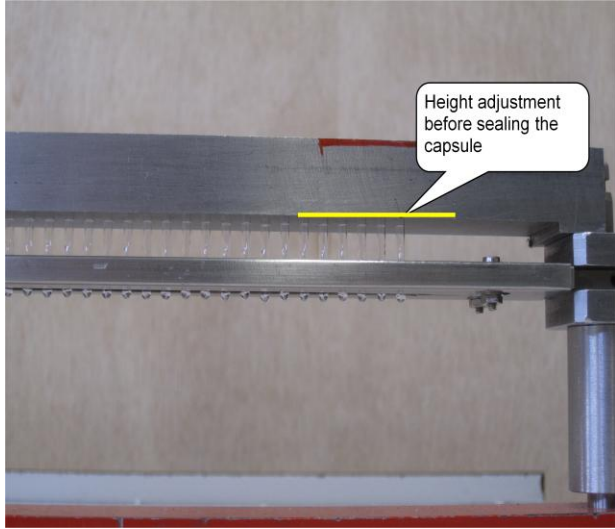


Figure 2

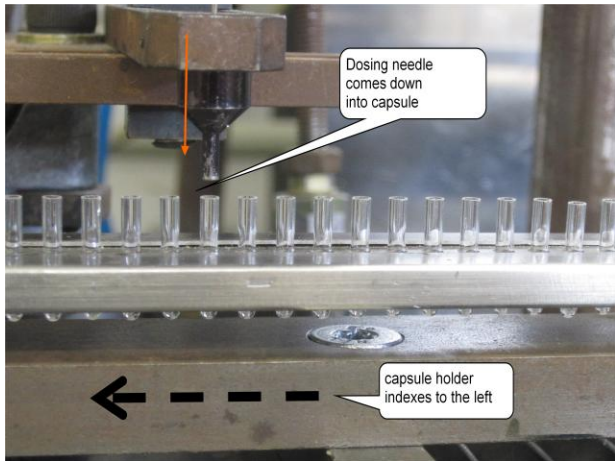


Figure 3

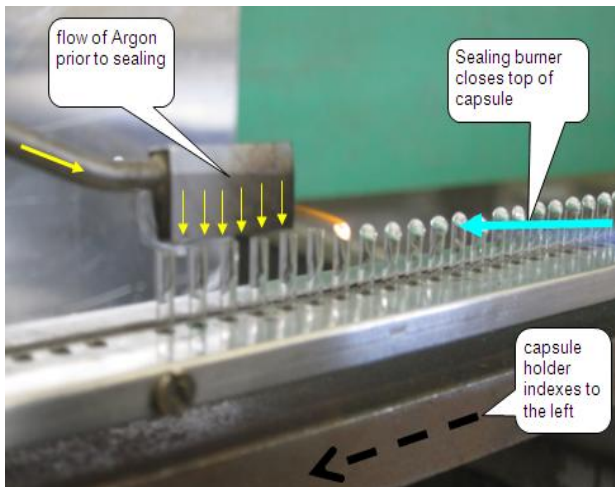


Figure 4

Checking the Hg pill

The sealed Hg pills are taken into a vibration seeder which takes each pill through a sensor. The seeder only passes pills with a certain diameter (Figure 6). The sensor reports a change in the electrical field when Hg is detected or not. If so, it ends in the bag 'OK'. Otherwise, it ends in the bag 'not OK' (Figure 8)



Figure 5

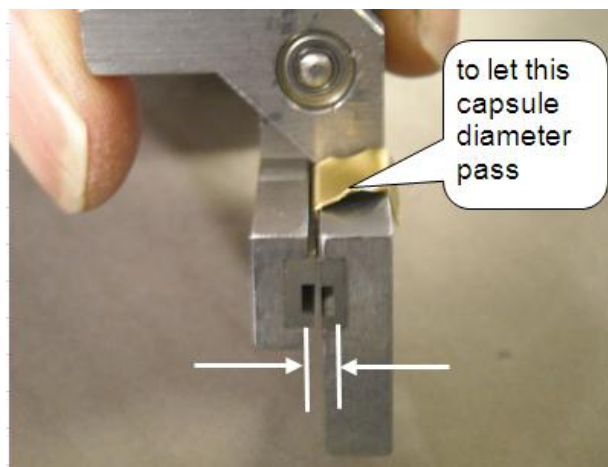


Figure 6

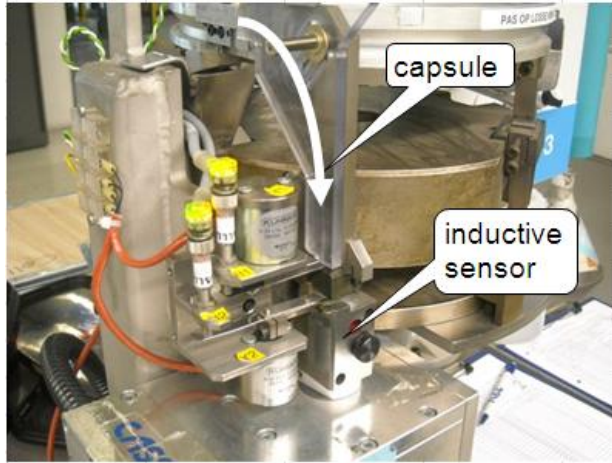


Figure 7

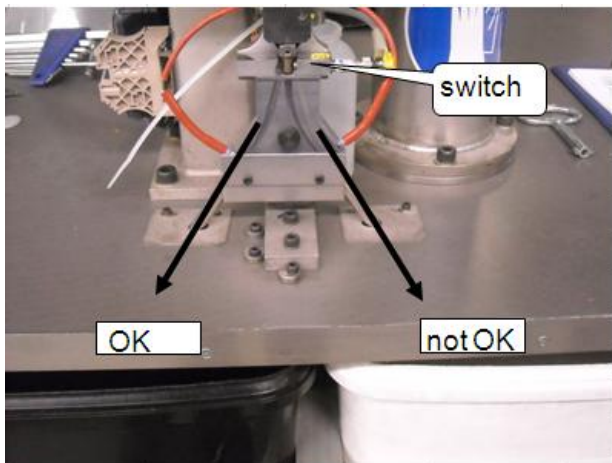


Figure 8

Statistical variation between Hg pills

Two batches of pills have been made by Philips Lighting in Roosendaal (The Netherlands). One batch contained pills having a nominal value of 1 mg and a second batch contained pills having a nominal value of 3 mg. Figure 9 shows the Hg content gained by weighing the pills before and after filling them with Hg; of some of those pills.

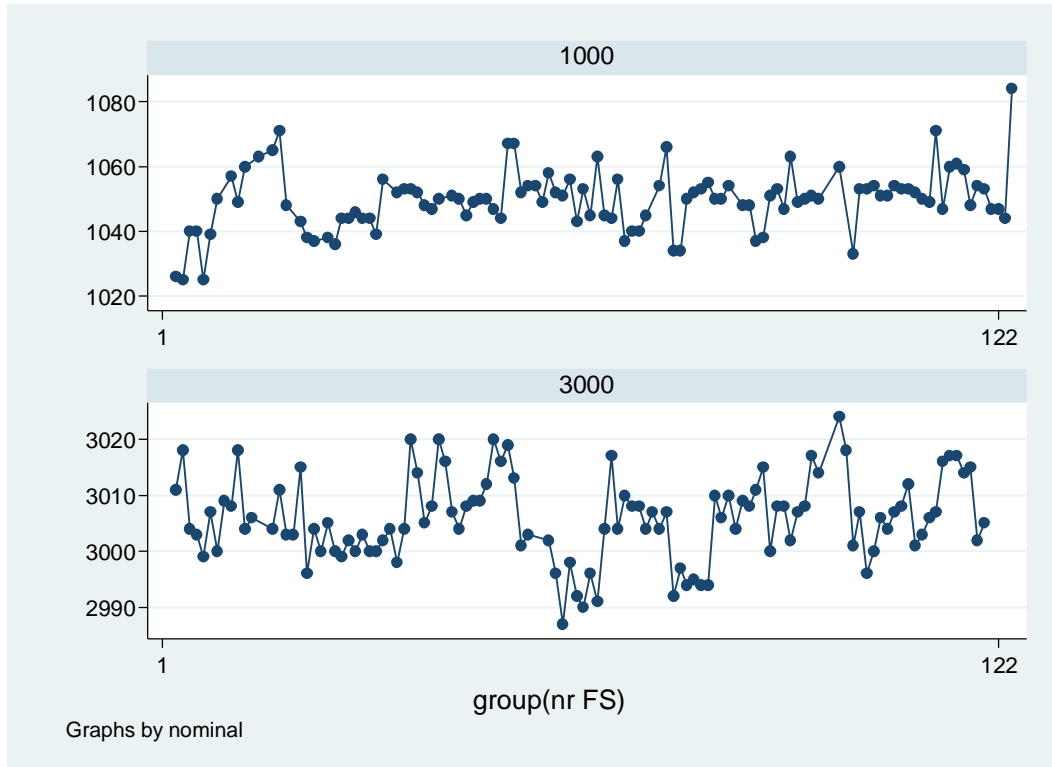


Figure 9. Hg-content of pills from the two batches

Figure 9 shows that the production of 1 mg pills is a much more stable process than the production of 3 mg pills is. The latter shows a more batch wise production where in the second half of the graph it seems that pills are produced in sub-batches of about 6 pills each. If time information is neglected and all data are analysed together the distribution of the measurements per group shows a normal distribution. Table 2 shows statistical information on these measurements.

Group	Obs	Mean	Std. Err.	Std. Dev.	[95% Conf. Interval]	
1000	110	1049.609	.8908857	9.343688	1047.843	1051.375
3000	112	3005.875	.7007218	7.415743	3004.486	3007.264
combined	222	2036.554	65.79609	980.3397	1906.886	2166.222

Table 2 Summary of Hg-content gained by weighing the pills before and after filling them with Hg.

A test on the equality of the two within “group standard deviations” rejects this hypothesis at the 5% level ($F([109;111]=1.59, p=0.016)$). This means that for the two groups separate standard deviations have to be used in what follows. It has however not been expected that the standard deviation of the 3 mg pills would turn out to be lower than the standard deviations of the 1 mg pills.

Table 2 also shows 95% confidence intervals for the mean of both batches. Laboratories have received pills (and lamps that were made by using these pills) taken at random from these batches. Since all measurements performed by these laboratories were destructive, measurement variation as shown by these laboratories have to be corrected for the initial variation between pills as shown in Table 2. A two

sided 95% confidence interval for the variances of the measurements on the pills is shown in Table 3. Measurement variation as obtained by the laboratories has to be corrected for the initial variation in order to estimate the variation introduced by each laboratory. The next section will discuss this in detail.

Group	std.Dev	Variance	[95% Conf. Interval]	
1000	9.34	87.2	68	116
3000	7.42	55.1	43	73

Table 3 95% confidence intervals for variation within groups, between pills

Each participating laboratory is represented by a letter to keep the individual results anonymous. All participants have received their own corresponding letter so they can track back their own results.

5. Statistics on inter laboratory results

Analysing the laboratory measurements

Methodology

All laboratories received a number of pills and a number of lamps for each method they would like to test. Laboratories have received pills (or lamps made from these pills) taken at random from the batches. Measuring the Hg-content in a pill or in a lamp is a destructive method; therefore pills and lamps cannot be measured more than once. The variation between pills/lamps obtained from a single analysis method has therefore an expected lower bound equal to the variation of Hg-content in the batch of pills used. An estimate of this lower bound can be found in Table 2. For a single method and a single laboratory the variation between measurements can be written as,

$$\sigma_{measurements}^2 = \sigma_{method}^2 + \sigma_{product}^2 \quad (1)$$

In this, a “product” can be a pill or a lamp. The major interest lies in the variance of the method. That is the variation one would see if it is possible to measure the same product over and over again. In order to estimate that variance the variation between products has to be subtracted from the observed variation. A next step of comparing standard deviations is to generate, say 95%, confidence intervals for the population standard deviations. This can be done using a method introduced by Welsch¹. It is known however that this method gives very unreliable results if the number of measurements used to estimate the standard deviation is very small. Although that is the case for the measurements (N≈5) intervals will still be calculated but need therefore to be interpreted with care..

Initial data analysis.

Figure 10 and Figure 11 show raw measurements. Horizontal lines in each graph show the average values of the Hg-contents as measured in the pills before distributing them among the laboratories as pills or lamps. These average values can be found in Table 2. Figure 10 and Figure 11 show for each “laboratory, method and technique” combination, their measurements as one group. The first thing that meets the eye is some severe outlying values. In Figure 10 at least four of those outliers are clearly visible and at least two are visible in Figure 11. Raw data can be found in Table 4. For each laboratory, method and technique combination it shows the minimum, maximum, mean, standard deviation and number of measurements. For some it shows the results before and after (between brackets) deleting ‘severe’ outlying observations. The final three columns show,

$$S = \sqrt{S_{measurements}^2 - S_{pills}^2} \quad (2)$$

$$BIAS = Mean_{measurements} - Mean_{pills} \quad (3)$$

$$RMSE = \sqrt{Bias^2 + S^2} \quad (4)$$

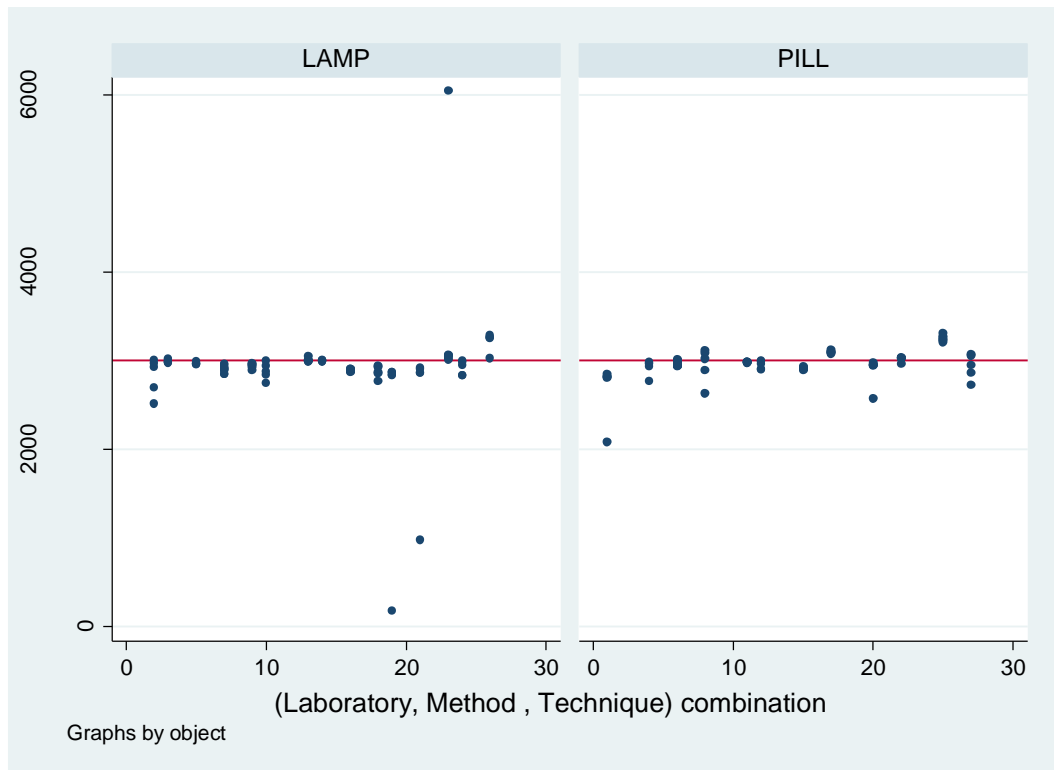


Figure 10 Raw measurements for 3000 ug Hg nominal. Horizontal line is drawn at the average found in Table 2

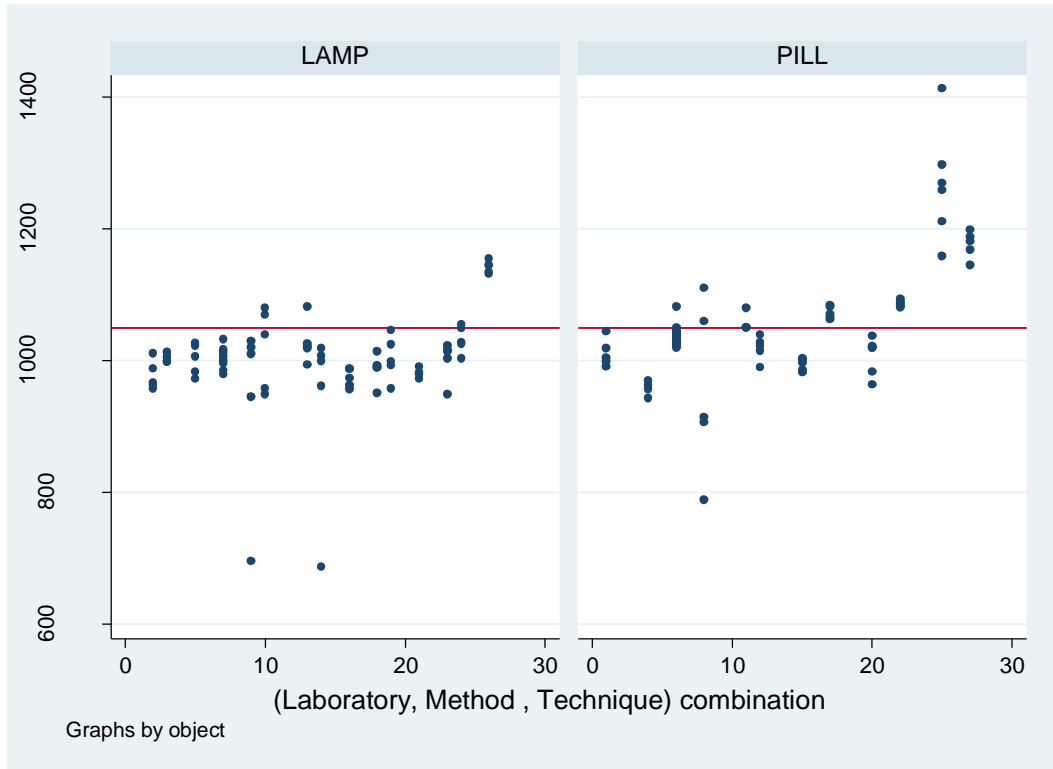


Figure 11 Raw measurements for 1000 ug Hg nominal. Horizontal line is drawn at the average found in Table 2

RMSE measures the sum of the structural and random differences between what has been measured and what the outcome is expected to be. Looking at Table 4 it can be seen that some of the laboratories produce an S that is undefined ($S < 0$) since $S_{measurements}^2 < S_{product}^2$. In that situation the 'best' point-estimate for that measurement variation is equal to $S_{measurements}^2 = 0$.

LAMPS, 3 mg						Std	Mean	S	BIAS	RMSE	
Method	min	mean	max	std	N						
1	alternative; small volume FL	2516	2825	3008	210	5	7.4	3005.9	210	-180.7	277.0
2	cold spotting	2976	2997	3025	19	5	7.4	3005.9	18	-9.1	19.8
3	Rinse methode for FL lamps	2957	2971	2997	15	5	7.4	3005.9	14	-34.5	37.1
4	cold spotting	2851	2908	2962	36	11	7.4	3005.9	35	-98.3	104.4
5	Rinse methode for FL lamps	2890	2940	2970	32	5	7.4	3005.9	31	-65.9	72.7
6	cold spotting	2750	2882	3000	95	5	7.4	3005.9	95	-123.9	156.3
7	Rinse methode for FL lamps	2994	3011	3053	24	5	7.4	3005.9	23	4.9	23.4
8	cold spotting	2997	3002	3007	4	5	7.4	3005.9	<0	-3.9	3.9
9	HNO3 injection method	2871	2889	2908	17	5	7.4	3005.9	15	-116.5	117.4
10	Rinse methode for FL lamps	2772	2875	2946	68	5	7.4	3005.9	68	-130.9	147.5
11	cold spotting	177(2837)	2319(2854)	2871(2871)	1197(19)	5(4)	7.4	3005.9	17	-151.9	152.9
12	cold spotting	983(2863)	2508(2890)	2924(1924)	853(30)	5(4)	7.4	3005.9	29	-115.9	119.5
13	Rinse methode for FL lamps	3016(3016)	3644(3045)	6044(3064)	1342(21)	5(4)	7.4	3005.9	20	39.1	43.8
14	cold spotting	2832	2921	3002	83	5	7.4	3005.9	83	-84.7	118.7
15	DIN IEC 62554 (5.3.4.2) + modified steps	3033	3221	3293	106	5	7.4	3005.9	106	215.5	240.2

LAMPS, 1 mg						Std	Mean	S	BIAS	RMSE	
Method	min	mean	max	std	N						
16	alternative; small volume FL	958	977	1011	22	5	9.3	1049.6	20	-72.2	74.9
17	cold spotting	998	1006	1013	7	5	9.3	1049.6	<0	-43.8	43.8
18	Rinse methode for FL lamps	973	1003	1027	24	5	9.3	1049.6	22	-47.0	51.9
19	cold spotting	979	1005	1033	15	11	9.3	1049.6	12	-44.9	46.4
20	Rinse methode for FL lamps	696(945)	940(1001)	1030(1030)	141(38)	5(4)	9.3	1049.6	37	-48.6	61.0
21	cold spotting	949	1019	1080	62	5	9.3	1049.6	61	-30.2	68.3
22	Rinse methode for FL lamps	994	1029	1082	32	5	9.3	1049.6	31	-21.0	37.4
23	cold spotting	687(962)	935(997)	1019(1019)	140(25)	5(4)	9.3	1049.6	23	-52.6	57.5
24	HNO3 injection method	957	974	988	14	5	9.3	1049.6	10	-75.8	76.5
25	Rinse methode for FL lamps	951	987	1014	23	5	9.3	1049.6	21	-62.2	65.6
26	cold spotting	958	1004	1046	33	5	9.3	1049.6	32	-45.4	55.6
27	cold spotting	973	981	991	6	5	9.3	1049.6	<0	-68.4	68.4
28	Rinse methode for FL lamps	949	1001	1023	30	5	9.3	1049.6	28	-48.4	56.2
29	cold spotting	1004	1032	1055	20	5	9.3	1049.6	18	-17.2	24.9
30	DIN IEC 62554 (5.3.4.2) + modified steps	1132	1142	1155	9	5	9.3	1049.6	<0	92.6	92.6

PILLS, 3 mg						Std	Mean	S	BIAS	RMSE	
Method	min	mean	max	std	N						
31	HNO3	2084(2809)	2678(2826)	2852(2852)	332(18)	5(4)	7.4	3005.9	16	-179.9	180.6
32	HNO3	2773	2926	2987	88	5	7.4	3005.9	87	-79.9	118.4
33	HNO3	2935	2969	3016	23	20	7.4	3005.9	22	-37.3	43.1
34	HNO3	2630	2950	3120	200	5	7.4	3005.9	199	-55.9	207.2
35	HNO3	2980	2986	2990	5	5	7.4	3005.9	<0	-19.9	19.9
36	HNO3	2903	2955	3000	46	5	7.4	3005.9	45	-51.1	68.4
37	HNO3	2894	2914	2938	17	5	7.4	3005.9	15	-92.3	93.5
38	HNO3	3082	3100	3121	14	5	7.4	3005.9	12	93.7	94.5
39	HNO3	2577	2894	2981	156	6	7.4	3005.9	156	-111.6	191.6
40	HNO3	2963	3019	3040	32	5	7.4	3005.9	31	12.9	33.2
41	HNO3	3212	3256	3311	35	6	7.4	3005.9	34	249.9	252.2
42	HNO3	2727	2934	3074	144	5	7.4	3005.9	143	-72.1	160.4

PILLS, 1 mg						Std	Mean	S	BIAS	RMSE	
Method	min	mean	max	std	N						
43	HNO3	991	1012	1044	21	5	9.3	1049.6	19	-38.0	42.3
44	HNO3	943	961	970	11	5	9.3	1049.6	6	-89.0	89.2
45	HNO3	1020	1038	1083	14	20	9.3	1049.6	10	-12.0	15.9
46	HNO3	789	956	1110	129	5	9.3	1049.6	129	-93.6	159.1
47	HNO3	1050	1056	1080	13	5	9.3	1049.6	10	6.4	11.6
48	HNO3	990	1019	1040	19	5	9.3	1049.6	16	-30.6	34.6
49	HNO3	982	994	1004	10	5	9.3	1049.6	3	-55.4	55.5
50	HNO3	1063	1073	1084	9	5	9.3	1049.6	<0	23.8	23.8
51	HNO3	964	1008	1038	28	6	9.3	1049.6	26	-41.8	49.5
52	HNO3	1081	1087	1094	5	5	9.3	1049.6	<0	37.4	37.4
53	HNO3	1159	1268	1413	86	6	9.3	1049.6	86	218.7	234.9
54	HNO3	1145	1176	1199	21	5	9.3	1049.6	18	126.8	128.1

Table 4 Raw data. Some entries show results after deleting an outlying observation.

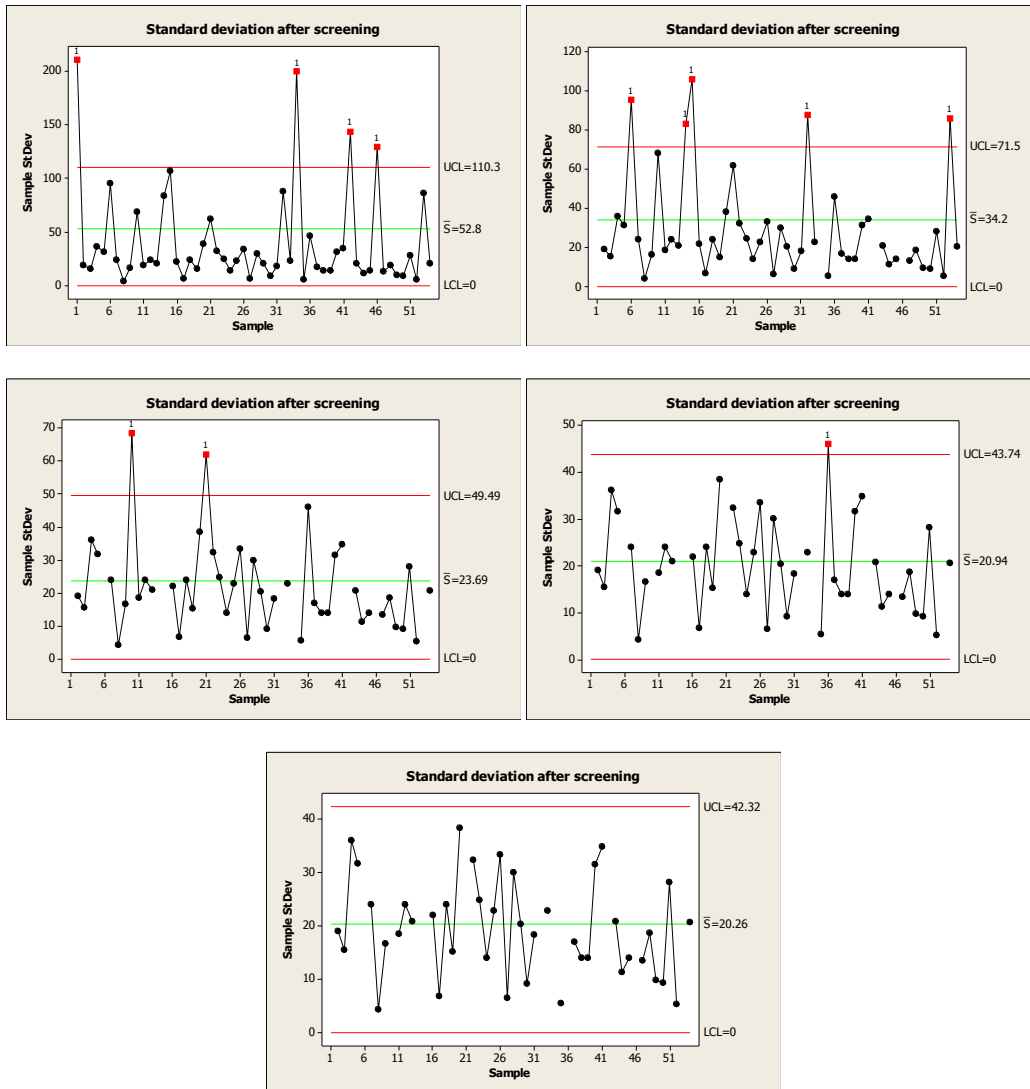


Figure 12 (a,b,c,d,e) Control charts for S. Note: Horizontal axis has no timeline interpretation.

Inference for total measurement variation

Calculating the “method standard deviation” is one thing, deciding if the real (unknown) population standard deviations differ between (laboratory, method, technique) combinations is another. One way on doing that is to set up a control chart over the 54 different standard deviations. Figure 12a-e shows some out-of-control situations. A control chart displays whether the data points can be seen as generated from a single stable process. In this situation it shows if all the standard deviations can be seen as coming from a single measurement process. If points are above the horizontal lines they can be seen as generated by a different measurement process than the rest of the data points. In the first graph this is true for index number 1, 34, 42 and 46. If these standard deviations are deleted and a new graph (Figure 12b) is made, there are still a number of special standard deviations (6, 14, 15, 32 and 53). One

can continue this until all data points fall between the two horizontal lines. A list of all laboratories generating out-of-control standard deviations can be found in Table 5. When making these graphs it was assumed that all standard deviations were based on 5 observations. This is not correct for some of the data points. It is expected however that this assumption does not influence the final conclusion in a severe way. It is assumed that the laboratory-method combination as listed in Table 5 generates standard deviations which are systematically too high compared to the rest of the standard deviations. These other standard deviations can be seen as generated by the same measurement process, meaning that the differences between them can be classified as random error or sampling error. The laboratories listed in Table 5 are good candidates for improvement actions on their measurement system.

Reference number	Object	Series	Method
1	Lamp	I	Alternative; small volume FL
6	Lamp	I	cold spotting
10	Lamp	I	Rinse method for FL lamps
14	Lamp	I	cold spotting
15	Lamp	I	DIN IEC (5.3.4.2) + modified steps
21	Lamp	II	cold spotting
32	Pill	III	HNO3
34	Pill	III	HNO3
36	Pill	III	HNO3
42	Pill	III	HNO3
46	Pill	IV	HNO3
53	Pill	IV	HNO3

Table 5 Out-of-control measurement standard deviations.

Inference for variation due to method alone

Equations 2-4 describe how this variation due to measurement method is calculated. As described in a previous section the result can be found in Table 4 in the column labelled 'S'. Table 6 shows the point estimates and 95% confidence intervals using Welsch' method. Some of them are grey. That is because the estimate of the standard deviation is 0 (zero) and no interval can be generated. Some others show a * where a number is expected. Those stars arise because the algorithm is not able to generate a result because of the specific input data. Figure 13 is the graph made from the results from Table 6. Although the confidence intervals are very rough it can still be seen that the intervals of some standard deviations do not overlap those of others which means that there are significant differences between the estimated standard deviations of the different methods.

LAMPS 3 mg				LAMPS 1 mg				PILLS 3 mg				PILLS 1 mg			
nr	Lower	point	Upper	nr	Lower	point	Upper	nr	Lower	point	Upper	nr	Lower	point	Upper
1	131	210	513	16	11	20	31	31	9	16	26	43	10	19	27
2	10	18	30	17		0		32	54	87	209	44	*	6	*
3	7	14	19	18	13	22	38	33	16	22	32	45	6	10	13
4	25	35	60	19	7	12	14	34	124	199	487	46	80	129	310
5	18	31	69	20	22	37	81	35		0		47	3	10	6
6	59	95	229	21	38	61	140	36	28	45	103	48	8	16	21
7	13	23	45	22	18	31	63	37	8	15	23	49	*	3	*
8		0		23	13	23	40	38	6	12	15	50		0	
9	8	15	22	24	4	10	6	39	100	156	341	51	16	26	49
10	42	68	160	25	11	21	33	40	18	31	68	52		0	
11	9	17	29	26	19	32	66	41	21	34	73	53	55	86	184
12	17	29	63	27		0		42	89	143	348	54	10	18	27
13	11	20	35	28	17	28	56								
14	52	83	198	29	10	18	26								
15	66	106	256	30		0									

Table 6 95% confidence intervals for measurement std. dev based on Welsch'method

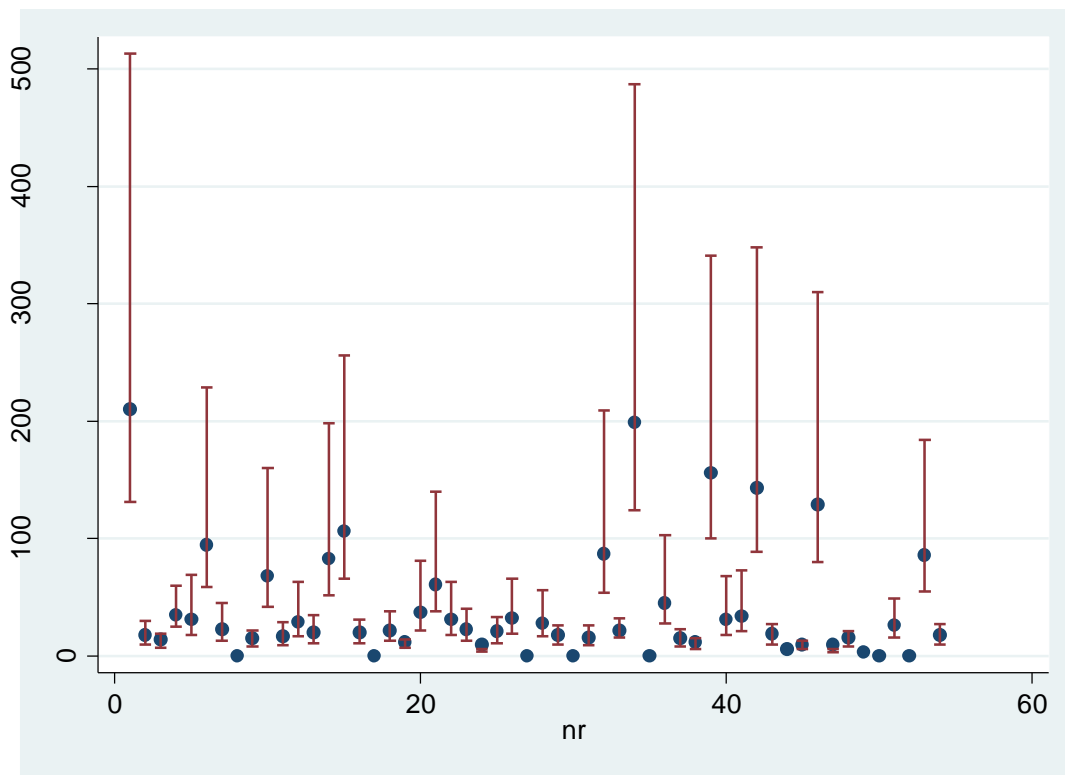


Figure 13 Graphical display of table 4. Vertical axis show approximate 95% confidence intervals for the standard deviation of the (Laboratory, method) combination. Numbers along horizontal axis correspond to the index in Table 5.

Comparing measurement methods

In total six different measuring methods have been used by the different laboratories. Figure 14 shows the measurement standard deviations. For some methods just one standard deviation is available. Testing the hypothesis that the population standard deviations for lamps are all the same using a one-way Analysis-of-Variance on the values of $\log(S)$ shows no significant results ($\alpha=0.05$).

Since the “cold-spotting method” (COLD) and the “rinse method” (RINSE) are the most important ones these two have been analysed without the other three methods. It can be shown that the median of the four distributions does not depend on Nominal values (1, 3 mg) nor on the method used. The standard deviations of the four distributions, as shown in the upper part of Figure 14, do depend on “method” alone ($p=0.051$). That means that on average the measurement spread does not depend on the method but that the variation in the results due to variation between laboratories is larger for the “cold-spotting method” than it is for the “rinse method”.

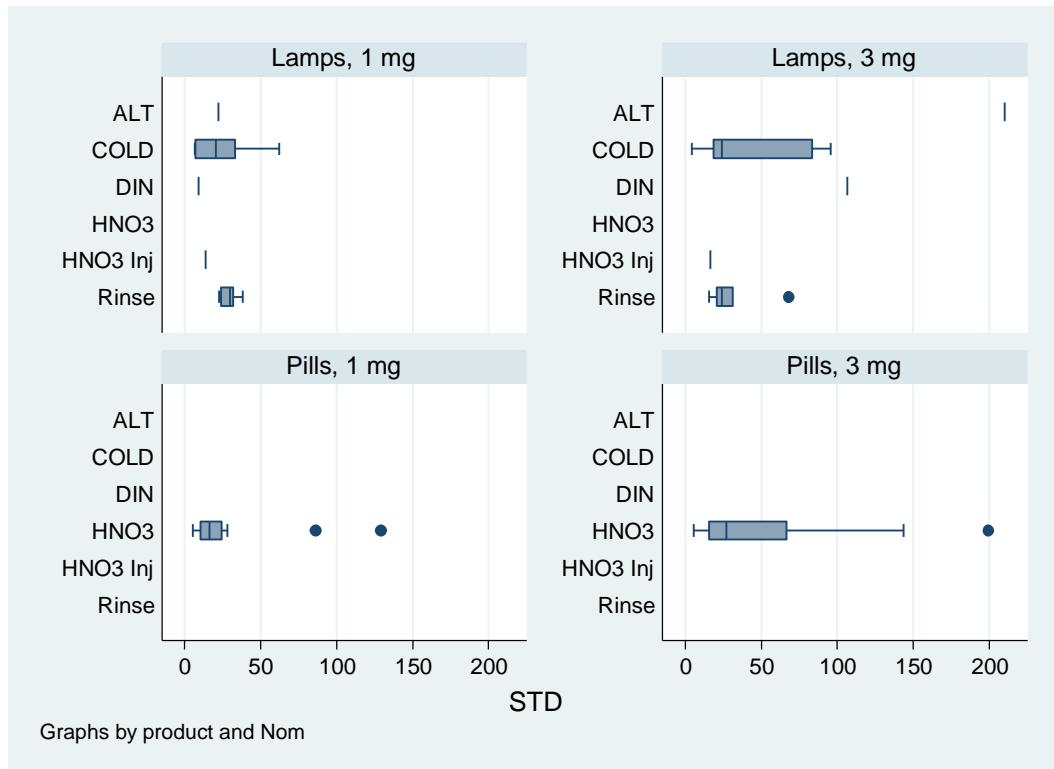


Figure 14 Box plots of measurement standard deviations. Single bars represent just one observation. Each Box-plot for COLD (=Cold spotting) is based on 7 observations, Rinse (=Rinse method for SL lamps) on 5 observations, while for pills the HNO3 boxplots are based on 12 observations each.

6. Conclusion and follow-up

- Aiming at improvement
 - In total 54 different “laboratory, method and technique” combinations delivered raw measurement variation information. Based on the control-chart technique a sub set of 12 of those combinations, 6 for lamps and 6 for pills, showed out-of-control results. See Table 5 for more details. These can be seen as situations where special causes could be present that have increased the standard deviations.
- Best Method
 - For pills only one method has been used (HNO₃) therefore the question about what method is best for determining the Hg-content in pills is trivial. For lamps three out of five methods delivered just a single standard deviation. In testing differences between in standard deviation between different methods no significant results have been found. Bear in mind that the power of this test is very low due to the fact that some methods delivered just a single value for their standard deviation. (see Figure 14)
 - Analyzing the two most important methods (cold-spotting method and rinse method) shows that on average a difference in measurement spread cannot be shown but that the variation in this measurement variation from laboratory to laboratory is the lowest for the “rinse method”. Laboratories produce more consistent results with the “rinse method” than they produce with the “cold-spotting method”.
- Hg-measurements between pills show larger standard deviations than expected.
 - When designing the test it was expected that the standard deviation in Hg-content between different pills (before distributing the pills and lamps to the participants) would be much lower than the standard deviations as measured by the different laboratories. This is not the case. In some situations laboratories provided standard deviations lower than the average deviation as measured before distribution. Therefore the laboratory results had to be corrected for initial variation between pills. Since it was not known which pills ended up in each laboratory only an average correction could be performed leading to ‘large’ uncertainty in the actual variation introduced by the different methods.

7. References

Chapter	Source
1A	Directive 2002/95/EC on the Restriction of the use of certain Hazardous Substances in Electrical and Electronic Equipment (RoHS)
1B	COMMISSION REGULATION (EC) No 245/2009 implementing Directive 2005/32/EC of the European Parliament and of the Council with regard to ecodesign requirements for fluorescent lamps etc. (requires labeling as X.X mg)
1C	IEC 62321 Ed.1: Electrotechnical products - Determination of levels of six regulated substances (lead, mercury, cadmium, hexavalent chromium, polybrominated diphenyls, polybrominated diphenyl ethers)
1D	prIEC 62554 Ed.1: Measurement of mercury level in fluorescent lamps (CD status)
1E	The ELC Guidance Document on Market Surveillance for the RoHS Directive (2002/95/EC), 28 June 2007, www.elcfed.org
3A	62554/CDV (IEC): "SAMPLE PREPARATION FOR MEASUREMENT OF MERCURY LEVEL IN FLUORESCENT LAMPS"
6A	Welsch B L, On the Linear Combinations of Several Variances, J. Am. Statist. Assoc., vol 51, pp 132-148, 1956
