The reliability of mercury analysis in environmental materials.

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Introduction

Mercury occurs in nature in its native elemental as well as in different mineral forms. It has been mined for centuries and is used in many branches of industry, agriculture and medicine. Mercury is very toxic to man and reports of poisoning due to the presence of the element in fish and shellfish caught at Minamata and Niigata, Japan have led not only to local investigations but to multi-national research into the sources and the levels of mercury in the environment[1].

The concentrations at which the element has to be determined in these studies are extremely small, usually of the order of a few parts in 10^9 parts[x] of environmental material.

Few analytical techniques provide the required sensitivity for analysis at such low concentrations, and only two are normally used for mercury: neutron activation analysis and atomic absorption photometry. They are also the most convenient end points of various separation schemes for different organic mercury compounds. Mercury analysis at the ppb-level is beset with many problems: volatility of the metal and its compounds, impurity of reagents, interference by other elements and many other analytical difficulties may influence the results. To be able to draw valid conclusions from the analyses it is necessary to know the reliability attached to the values obtained.

To assist laboratories in the evaluation of their analytical performance, the International Atomic Energy Agency through its own laboratory at Seibersdorf has organised already in 1967 an intercomparison of mercury analysis in flour[2]. Based on the results obtained at that

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x) The corresponding concentration unit is the "ppb" (parts per billion). Billion is used in the American sense (10^9) in this expression.

time, a whole series of intercomparisons of mercury determinations in nine different environmental materials was undertaken in 1971. The materials investigated included corn and wheat flour, spray-dried animal blood serum, fish solubles, milk powder, saw dust, cellulose, lacquer paint and coloric material. All the materials were homogenized, their homogeneity checked by various techniques, sometimes involving comparisons of trace element spectra of sub-samples, and sent to the participating laboratories. Each laboratory received one or several 10g sub-samples of each material which it wanted to analyse.

Results

23 laboratories took part in the series of intercomparisons; most of them, however, analysed only a few of the materials provided. One laboratory submitted two different sets of results which were treated separately, as if received from two different laboratories, so that altogether 24 different series of results were available for evaluation. These results are presented, separately for each item, in Tables I to IX. Laboratories are entered by code numbers the sequence of which does not correspond to the sequence of participants in the list provided in the Annex.

Laboratories reported results of individual determinations as well as averages of these. The number of individual determinations which went into each average is given in column 2, the average itself, expressed in ppb Hg, in column 3. In general, this average has been calculated by the laboratory itself and has been put into the table as received, without any change. This is the reason for the different number of significant figures of the entries in this column. Only when concentration units other than ppb were used, these were corrected for the sake of uniformity. Also, in one or two cases, obviously erroneous calculations of the average from the individual determinations were put right. Standard deviations and standard errors, given in columns 4 and 5, were calculated according to accepted procedures. In the calculation of the overall mean of "accepted" laboratory averages, all values outside of the mean plus or minus three standard deviations were excluded. Also excluded were, of course, all values which represented upper limits of concentrations. This exclusion principle is somewhat more stringent than the method of Graf and Henning[3] or that of Chauvenet[4] which have been used in other intercomparisons organised by the Agency[5,6] and which, for the small number of values available in each of the intercomparisons, was

considered to allow too much scatter. Based on the mean of the accepted values, the deviations of individual averages from this mean were calculated. They can be found in column 7 in juxtaposition to the accuracy estimates provided by the laboratories themselves. In line with experience obtained in other, earlier intercomparisons, little, if any, correlation exists between the two sets of numbers.

Finally, column 8 gives information on the methods used in the determinations. Roughly two thirds of the values were obtained by neutron activation analysis, one third by atomic absorption photometry. Only two values out of 87 were obtained by a colorimetric method. Fig's 1 to 9 show the same results in graphical form. The overall mean of all accepted values is shown by a large dotted line drawn across the chart, individual laboratory averages are represented by short horizontal lines. The standard deviation s and the standard error $\bar{s}$ of each laboratory average are shown by thin and by thick vertical lines, respectively. Results which were obtained from single measurements are marked with crosses, those which would lie outside of the boundaries of the figure are marked by arrows pointing towards the edge of the drawing.

Table X summarizes the results of all nine intercomparisons, showing the total number of individual values and of laboratory averages received, the number of those inside the limits of three standard deviations from the mean earlier defined as acceptable and the number outside these limits which could not be used in further calculations. The range of accepted values is given and can be compared with the total range of all laboratory averages. Finally, the overall mean of all accepted averages is given together with its standard deviation.

Discussion

Of all results received a full third was found to lie outside the limits of plus or minus three standard deviations from the overall mean. This emphasizes the need for caution when results of mercury determinations in environmental materials are used to calculate concentration levels or to establish relations between such concentrations and their supposed sources. Not surprisingly, the standard deviations of the overall means of mercury concentrations in the different materials investigated were also found to be rather high, ranging from 23% to 65%, even though only the closer two thirds of all laboratory averages were used in their estimation. Correspondingly large was the range of accepted values,

with the ratio of the upper to the lower limit of this range varying from 1.6 for lacquer paint to 7.9 for corn flour. Expressed as percent of the overall mean the shortest range (that for lacquer paint) extended from 74% to 120% of the mean for that material, the longest (for corn flour) from 24% to 187%. That means that if the evaluation of the mercury content in the corn flour sample had been based on only one laboratory, even out of those who turned in "accepted" results for this material, it would have easily been possible to arrive at a figure equal to either one quarter of or to twice that of the mean value listed.

Somewhat unexpectedly, no correlation was found between the order of magnitude of the mercury content in the different materials which varied from 4.5 ppb in milk powder to 75 ppb in cellulose, and the reliability of the analyses. Standard deviations and ranges of accepted values differed with different materials without any apparent dependence on the absolute concentration within the range of concentrations studied. Also, as can be learned from Table XI which separates results according to the analytical method used, no significant difference in performance between the two methods mainly employed, viz. atomic absorption photometry and destructive neutron activation analysis could be detected.

Conclusions

The intercomparisons described here have shown that the reliability of mercury analysis in environmental materials at levels of 5 - 100 ppb of mercury leaves much to be desired. Even when consideration is limited to those two thirds of the values which show the least scatter, standard deviations are still of the order of fifty percent of the mean value. These findings underline the need for continuous control of the quality of analytical work in this field which may be achieved by the use of standard reference materials or by repeated intercomparisons.

REFERENCES

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TABLE I

DETERMINATION OF MERCURY IN CORN FLOUR
INTERCOMPARISON RUN V-1

Lab. No.	Number of determinations	Laboratory average (ppb)	Standard deviation of laboratory mean s ±(ppb)	Standard error of laboratory mean $\bar{s}$ ±(ppb)	Accuracy: Laboratory's own estimate ± (%)	Accuracy: Actual deviation from mean (%)	Method used b)
1	4	2.45	0.2	0.1	15	-76.2	1
2	3	2.6	0.5	0.3	10 - 15	-74.4	1
3	4	4.6	0.5	0.2		-54.7	1
4	6	8	3.5	1.4	64	-23.7	2
5	4	8.7	2.6	1.3		-15.7	1
6	2	11.4	2.0	1.4		+11.1	2
7	1	17			12	+65.6	1
8	6	18.4	1.0	0.4	10	+79.4	1
9							
10	6	19.3	1.8	0.7	20	+88.0	1
11	6	37 a)	1.9	0.8	12	+266	1
12	4	55 a)	2.2	1.1	50	+436	1
13	5	173 a)	27.5	12.3	15	+580	3
14	6	< 10 a)			95 - 98		2
15	4	< 20 a)					1
16	6	200 a)	98.3	40.2		+1870	2
17							
18							
19							
20							
21							
22							
23							
24							

Overall mean of all accepted laboratory averages 10.3 ± 6.6 pp Hg

a) Result not used in calculation of overall mean

b) The following codes are used:
1 = destructive activation analysis
2 = atomic absorption
3 = colorimetry

TABLE II

DETERMINATION OF MERCURY IN WHEAT FLOUR
INTERCOMPARISON RUN V-2

Lab. No.	Number of determinations	Laboratory average (ppb)	Standard deviation of laboratory mean s ±(ppb)	Standard error of laboratory mean $\bar{s}$ ±(ppb)	Accuracy: Laboratory's own estimate ± (%)	Accuracy: Actual deviation from mean (%)	Method used [b]
1	3	< 1 a)					1
2	3	2.5	0.4	0.2	10-15	-45	1
3	4	40.2 a)	11.2	5.6	100	+780	1
4	5	2				-56	2
5							
6	1	4.9				+7.4	2
7	1	4.7			53	+3.1	1
8	4	7.75	2.2	1.1	20	+70	1
9	6	7.03	3.3	1.4	20	+54	1
10	6	3.03	0.6	0.2	20	-33	1
11	6	57 a)	11.5	4.7	7	+1140	1
12	6	43 a)	1.7	0.7	50	+ 840	3
13	3	74 a)	11.0	6.4	15	+1520	2
14	6	< 10 a)			95-98		1
15	4	< 20 a)					1
16							
17							
18							
19							
20							
21							
22							
23							
24							

Overall mean of all accepted laboratory averages 4.6 ± 2.2 pp Hg

a) Result not used in calculation of overall mean

b) The following codes are used:
1 = destructive activation analysis
2 = atomic absorption
3 = colorimetry

TABLE III

DETERMINATION OF MERCURY IN ANIMAL BLOOD SERUM
INTERCOMPARISON RUN A-2

Lab. No.	Number of determinations	Laboratory average (ppb)	Standard deviation of laboratory mean s ±(ppb)	Standard error of laboratory mean $\bar{s}$ ±(ppb)	Accuracy: Laboratory's own estimate ± (%)	Accuracy: Actual deviation from mean (%)	Method used [b]
1							
2							
3	4	7.5	2.5	1.3		-42.3	1
4							
5	4	15.6	2.5	1.3		+20.0	1
6	3	4.1	0.3	0.2		-68.5	2
7							
8	6	12.5	1.7	0.7	10	- 3.8	1
9							
10	6	21.6	1.6	0.7	20	+66.2	1
11	4	49 a)	1.5	0.8	12	+277	1
12	4	40 a)	10.1	5.1	50	+208	1
13							
14							
15							
16							
17	5	20	7.1	3.2	150	+53.8	2
18	5	12.8	3.3	1.5	26	- 1.5	1
19							
20							
21							
22							
23							
24	2	9.5	2.1	1.5	10	-26.9	1

Overall mean of all accepted laboratory averages 13.0 ± 6.0 ppb Hg

a) Result not used in calculation of overall mean

b) The following codes are used:
1 = destructive activation analysis
2 = atomic absorption

TABLE IV DETERMINATION OF MERCURY IN FISH SOLUBLES
INTERCOMPARISON RUN A-6

Lab. No.	Number of determinations	Laboratory average (ppb)	Standard deviation of laboratory mean s ±(ppb)	Standard error of laboratory mean $\bar{s}$ ±(ppb)	Accuracy: Laboratory's own estimate ± (%)	Accuracy: Actual deviation from mean (%)	Method used [b]
1							
2							
3	3	76.0	9.8	5.7		+21.4	1
4	3	83	5.8	3.4	12	+32.6	2
5	4	38.6	2.0	1.0		-38.3	1
6	2	150 a)	5.7	4.0		+140	2
7							
8	6	32.8	5.4	2.2	10	-47.8	1
9							
10	6	43.4	4.2	1.7	20	-30.6	1
11	4	65	1.7	0.8	12	+ 3.8	1
12	6	42	14.5	5.9	80	-32.9	1
13							
14							
15							
16							
17	5	48	4.5	2.0	60	-23.3	2
18							
19	6	208 a)	65.5	26.7	21	+232	2
20	3	73	7.0	4.0	95-100	+16.6	2
21	6	83.5	5.3	2.2		+33.5	2
22	6	300 a)	108.4	44.3		+383	2
23							
24	2	104	2.1	1.5	10	+66.0	1

Overall mean of all accepted laboratory averages 62.6 ± 23.1 ppb Hg

a) Result not used in calculation of overall mean

b) The following codes are used:
1 = destructive activation analysis
2 = atomic absorption

TABLE V

DETERMINATION OF MERCURY IN MILK POWDER
INTERCOMPARISON RUN A-8

Lab. No.	Number of determinations	Laboratory average (ppb)	Standard deviation of laboratory mean s ± (ppb)	Standard error of laboratory mean $\bar{s}$ ± (ppb)	Accuracy: Laboratory's own estimate ± (%)	Accuracy: Actual deviation from mean (%)	Method used [b]
1							
2							
3	4	2.3	1.5	0.7		-60.0	1
4							
5	4	5.1	3.0	1.5		+12.2	1
6	1	4.5				0.0	2
7							
8	5	4.79	1.2	0.5	20	+ 6.5	1
9	4	5.37	1.7	0.8	20	+19.3	1
10	6	13.6 a)	1.3	0.5	20	+202	1
11	4	8 a)	0.8	0.4	17	+77.8	1
12	6	24 a)	6.4	2.6	50	+434	1
13							
14							
15							
16							
17	6	< 20 a)			150		2
18							
19							
20	3	5	-	-	95-100	+11.1	2
21							
22							
23							
24	2	< 3 a)	-	-			1

Overall mean of all accepted laboratory averages 4.5 ± 1.1 ppb Hg

a) Result not used in calculation of overall mean

b) The following codes are used:
1 = destructive activation analysis
2 = atomic absorption

TABLE VI

DETERMINATION OF MERCURY IN SAW DUST
INTERCOMPARISON RUN S-8

Lab. No.	Number of determinations	Laboratory average (ppb)	Standard deviation of laboratory mean s ±(ppb)	Standard error of laboratory mean $\bar{s}$ ±(ppb)	Accuracy: Laboratory's own estimate ± (%)	Accuracy: Actual deviation from mean (%)	Method used [b]
1							
2	3	29.7	1.7	1.0	10	-28.4	1
3							
4	5	42	5.1	2.3	7	+ 1.2	2
5							
6							
7	1	49			57	+18.1	1
8	6	31.2	2.3	0.9	10	-24.8	2
9							
10							
11	6	267 a)	49.7	20.3	15	+541	1
12	5	41	10.5	4.7	80	- 1.2	1
13							
14							
15							
16							
17	6	123 a)	45.5	18.6	25	+195	2
18							
19							
20							
21							
22							
23	5	1922 a)	1766	790		+4530	4
24	2	56	23.3	16.5	10	+34.9	1

Overall mean of all accepted laboratory averages 41.5 ± 10.1

a) Result not used in calculation of overall mean

b) The following codes are used:
1 = destructive activation analysis
2 = atomic absorption
4 = non-destructive activation analysis

TABLE VII

DETERMINATION OF MERCURY IN CELLULOSE
INTERCOMPARISON RUN S-9

Lab. No.	Number of determinations	Laboratory average (ppb)	Standard deviation of laboratory mean $\pm s$ (ppb)	Standard error of laboratory mean $\pm \bar{s}$ (ppb)	Accuracy: Laboratory's own estimate $\pm$ (%)	Accuracy: Actual deviation from mean (%)	Method used [b]
1							
2	3	43.7	0.9	0.5	5	-41.5	1
3							
4	5	83	4.3	1.9	7	+11.4	2
5							
6							
7							
8	6	33.7	2.9	1.2	10	-55	1
9							
10							
11	6	143	13.7	5.6	15	+92.0	1
12	3	103	16.5	9.5	50	+38.2	1
13							
14							
15							
16							
17	6	47	16.3	6.7	60	-36.9	2
18							
19							
20							
21							
22							
23	5	608 a)	129.1	57.7		+715	4
24	4	68	1.4	0.7		- 8.7	1

Overall mean of all accepted laboratory averages 74.5 ± 38.7

a) Result not used in calculation of overall mean

b) The following codes are used:
1 = destructive activation analysis
2 = atomic absorption
4 = non-destructive activation analysis

TABLE VIII

DETERMINATION OF MERCURY IN LACQUER PAINT
INTERCOMPARISON RUN S-10

Lab. No.	Number of determinations	Laboratory average (ppb)	Standard deviation of laboratory mean $\pm s$ (ppb)	Standard error of laboratory mean $\pm \bar{s}$ (ppb)	Accuracy: Laboratory's own estimate $\pm$ (%)	Accuracy: Actual deviation from mean (%)	Method used [b]
1							
2	3	77.1	2.0	1.2	5	+6.6	1
3							
4	2	86	1.4	1.0	10	+19.0	2
5							
6							
7							
8	6	53.8	6.9	2.8	10	-25.6	1
9							
10							
11	6	247 a)	45.9	18.7	10	+242	1
12							
13							
14							
15							
16							
17	6	240 a)	6.3	2.6	13	+232	2
18							
19							
20							
21							
22							
23	6	500 a)	100.4	41.0		+606	4
24							

Overall mean of all accepted laboratory averages 72.3 ± 16.6

a) Result not used in calculation of overall mean

b) The following codes are used:
1 = destructive activation analysis
2 = atomic absorption
4 = non-destructive neutron activation analysis

TABLE IX DETERMINATION OF MERCURY IN COLORIC MATERIAL
INTERCOMPARISON RUN S-11

Lab. No.	Number of determinations	Laboratory average (ppb)	Standard deviation of laboratory mean $\pm s$ (ppb)	Standard error of laboratory mean $\pm \bar{s}$ (ppb)	Accuracy: Laboratory's own estimate $\pm$ (%)	Accuracy: Actual deviation from mean (%)	Method used [b]
1 2 3	3	29.4	1.4	0.8	5	+4.2	1
4 5 6 7	5	7.8	1.4	0.6	25	-75.0	2
8 9 10	8	30.4	7.9	2.8	15	-1.0	1
11 12 13 14 15 16	4	446 a)	25.8	12.9	7	+1350	1
17 18 19 20 21 22 23 24	6	55	13.8	5.6	50	+79.0	2

Overall mean of all accepted laboratory averages 30.7 ± 19.3

a) Result not used in calculation of overall mean

b) The following codes are used:
1 = destructive activation analysis
2 = atomic absorption

TABLE X Summary of Intercomparison Results

Material analysed		Corn flour	Wheat flour	Animal blood	Fish solubles	Milk powder	Saw dust	Cellu-lose	Lacquer paint	Coloric material	All inter-compa-risons
Intercomparison Code		V-1	V-2	A-2	A-6	A-8	S-8	S-9	S-10	S-11	
Number of reported results	individual determinations	67	58	43	62	45	39	38	29	26	407
	laboratory averages	15	14	10	14	11	9	8	6	5	92
Number of values accepted	individual determinations	36	26	35	48	21	22	33	11	22	254
	laboratory averages	9	7	8	11	6	6	7	3	4	61
Number of values excluded	individual determinations	31	32	8	14	24	17	5	18	4	153
	laboratory averages	6	7	2	3	5	3	1	3	1	31
Total range of laboratory averages (ppb)		2,45 - 200	2,5 - 74	4,1 - 49	32,8 -300	2,3 - 24	29.7 -1922	33,7 - 608	53,8 -500	7,8 -446	
Range of accepted laboratory averages (ppb)		2,45 -19,3	2,5 -7,75	4,1 -21,6	32,8 -104	2,3 -5,37	29,7 -56	33,7 -143	53,8 - 86	7,8 - 55	
Overall mean of accepted laboratory averages (ppb)		10,3	4,6	13.0	62,6	4,5	41,5	74,5	72,3	30,7	
Standard deviation of overall mean S	ppb	6,6	2,2	6,0	23,0	1,1	10,1	38,7	16,6	19,3	
	%	64,8	48,7	46,3	36,8	24,8	24,4	51,9	23,0	62,9	

TABLE XI Comparison of two analytical methods for Mercury

Intercomparison Run	Mercury content (ppb)	Total number of reported laboratory averages	Obtained by destructive neutron activation analysis			Obtained by atomic absorption		
			a) number reported	b) number excluded	c) ratio b/a (%)	a) number reported	b) number excluded	c) ratio b/a (%)
V-1, Corn flour	10.3	15	10	3	30	4	2	50
V-2, Wheat flour	4.6	14	10	5	50	3	1	33
A-2, Animal blood	13.0	10	8	2	25	2	-	0
A-6, Fish solubles	62.6	14	7	-	0	7	3	43
A-8, Milk powder	4.5	11	8	4	50	3	1	33
S-8, Saw dust	41.5	9	5	1	20	3	1	33
S-9, Cellulose	74.5	8	5	-	0	2	-	0
S-10, Lacquer paint	72.3	6	3	1	33	2	1	50
S-11, Coloric material	30.7	5	3	1	33	2	-	0
Total		92	59	17	29	28	9	32

Hg in CORN FLOUR; V-1

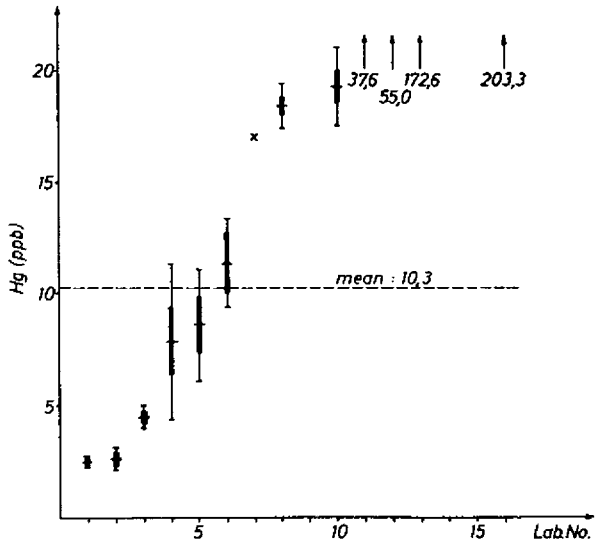

FIG. 1

Hg in WHEAT FLOUR; V-2

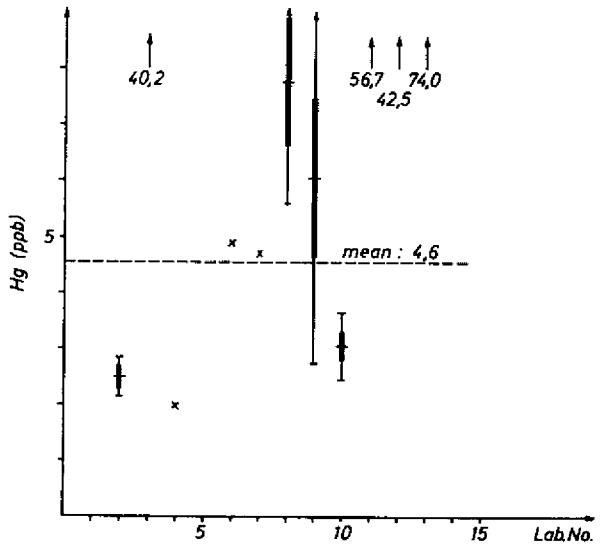

FIG. 2

Hg in SPRAY-DRIED ANIMAL BLOOD SERUM; A-2

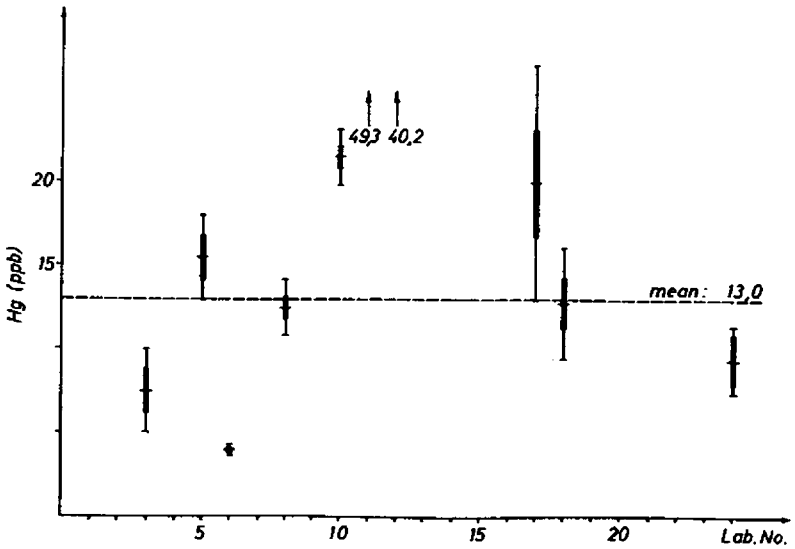

FIG. 3

Hg in FISH SOLUBLES; A-6

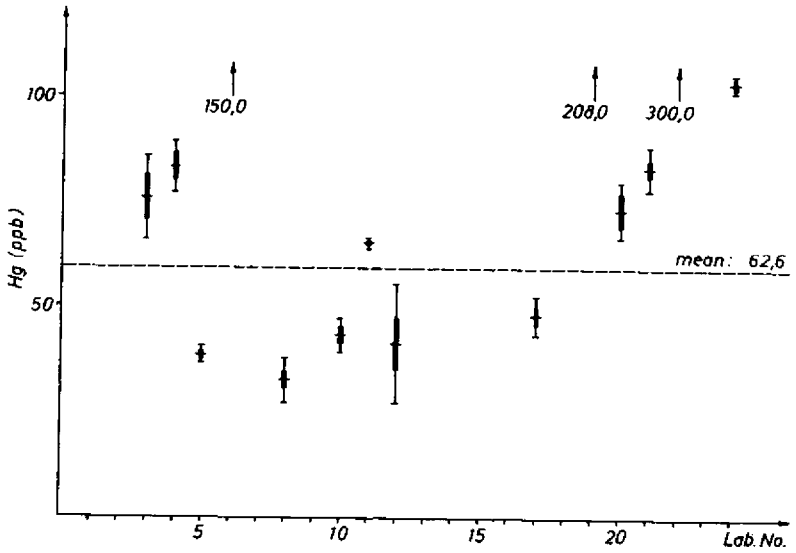

FIG. 4

Hg in MILK POWDER; A-8

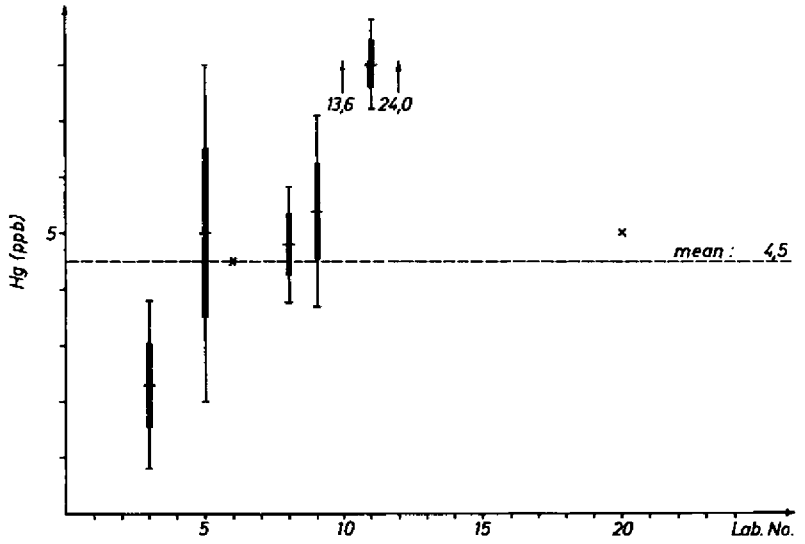

FIG. 5

Hg in SAW DUST; S-8

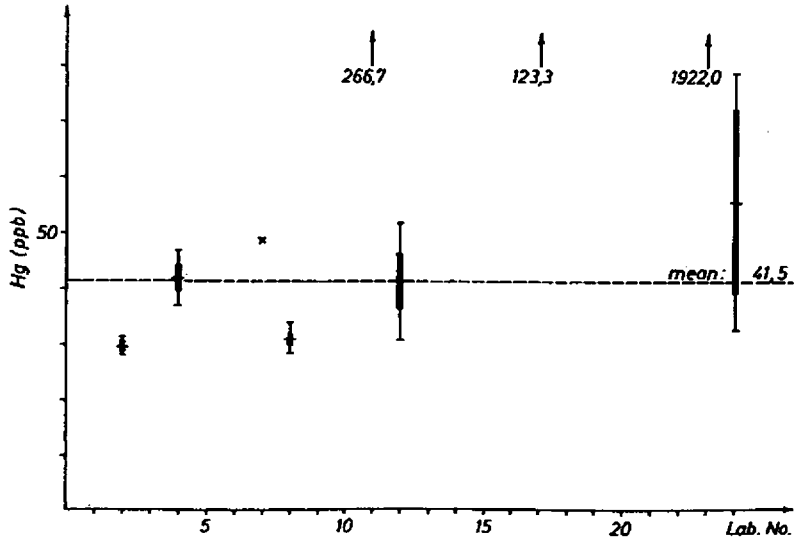

FIG. 6

Hg in CELLULOSE; S-9

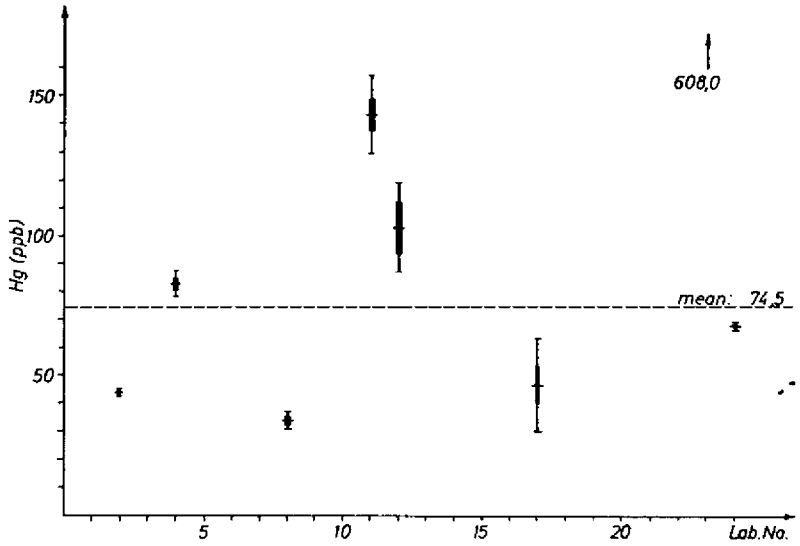

FIG. 7

Hg in LACQUER PAINT; S-10

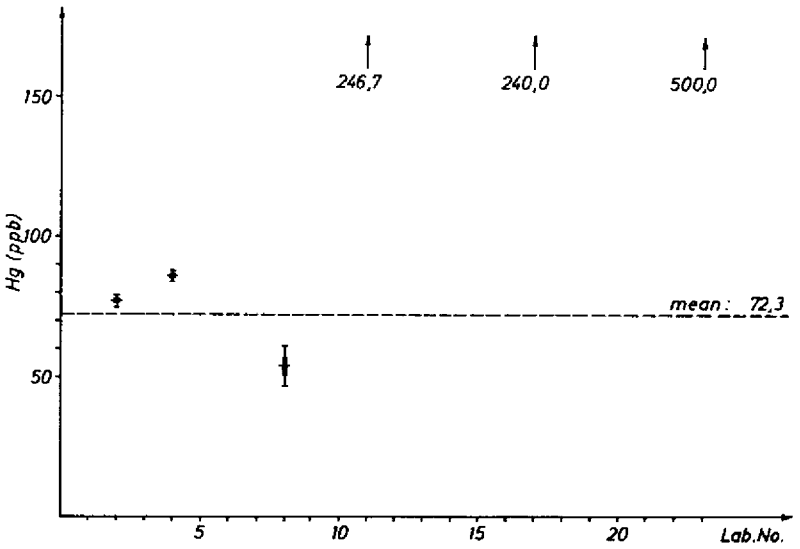

FIG. 8

Hg in COLORIC MATERIAL; S-11

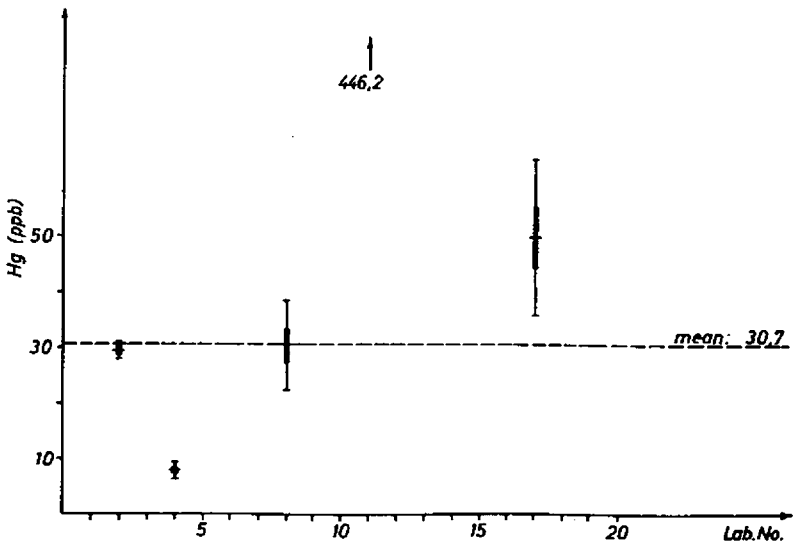

FIG. 9

ANNEX

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