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THE COLLECTION AND MEASUREMENT

of

AIRBORNE MERCURY-II

APCD 71 - 12

by

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ABSTRACT

This report is the second in the series of reports on the analysis of airborne mercury. The earlier report was issued on September 10, 1971 under the serial number APCD 71-8.

In this report some additional experience is given with the Casella personal sampler and the silver absorber. The collection efficiency of the silver absorber for metallic mercury is close to 100%. A recommended sampling procedure using the Casella sampler is suggested.

A limited survey of mercury levels in air has been made, from which it appears that ambient air background levels with the analytical method used can be as low as 5 nanograms per cubic metre of air. The measurement of mercury in air levels is being continued in order to accumulate as much background data as possible.

INTRODUCTION

This is the second in a series of reports on the Collection and Measurement of Airborne Mercury. The first in this series was APCD 71-8, dated September 10, 1971. The collection efficiency of the silver absorbers has been further evaluated and found to be excellent. The offscale sensitivity problem of the Du Pont 400 analyzer is being brought under control by means of an integrating digital voltmeter.

SAMPLE PREPARATION

Environmental samples may be organic or inorganic; examples are fish or river bottom mud. The three physical phases are represented in the form of the earth's crust, the world's water supplies and the lower atmosphere. Our interest is directed, at the moment, to air sampling and analysis. It is also expected we will be able to adapt the methods now being developed for air to the analysis of water.

The sample, of whatever kind, must of course be representative of the environment which is to be investigated, and it should be homogeneous within itself so that a sufficient number of aliquots may be analyzed to establish precision. The problem of heterogeneity is acute with biological samples such as fish and less acute with soil, mud, rock etc. Nevertheless, samples such as soil must be mixed carefully by approved sampling procedures. Sieving and grinding may be necessary. Naturally, with such heterogeneous samples, it is necessary to ensure that classification does not occur while endeavouring to make the sample homogeneous. It is normal to grind rock

samples to a uniform fineness before analysis so that for rock samples this decision may have been taken out of the hands of the analyst a priori. With soil samples, should one grind the entire sample and ensure representativeness by using the coal pile technique or should one sieve out the coarse rock particles? It is impracticable to prepare vegetation samples by other than grinding after air drying. How much mercury may be lost during air drying and how much may be lost during grinding? At this point, let us again point out that the sample must be representative when taken and remain representative during sample preparation. These error factors should be mentioned when analytical results for mercury are reported and, if possible, some estimate of their magnitude and direction should be given.

The problem of the representativeness of samples of airborne mercury is probably less complicated than for solid samples, particularly if the airborne mercury is in the form of vapor. This is likely to be the situation when mercury is liberated from chloralkali plants together with the escaping hydrogen. Assuming the airborne mercury to be in the vapor form, it is difficult to believe analytical data given in the literature based upon the analysis of air samples taken on high volume filters. In theory, at least, one would consider that the mercury should be sampled by means of reagents or materials which react with, chelate,or reliably fix the mercury. Various permanganate solutions have been used for this purpose. The effectiveness of such permanganate solutions will be briefly discussed later.

Whatever the form and composition of the original airborne mercury sample, some kind of sample treatment is required to separate

the mercury from the sample matrix and to get the mercury vapor into the measuring cell quantitatively. The prepared sample may be a liquid, which has been prepared by acid digestion. A conventional approach to the handling of such a sample is to add a reducing agent and to sweep the elemental mercury, so formed, into the measuring cell. In our hands, this reduction procedure, associated with the names of Hatch and Ott, gives a recovery of only 50% of the mercury present. This reduction procedure will be discussed in greater detail in a subsequent report. The present report will be based mainly upon the analysis of batch samples of air taken on the silver absorbers previously described. Mercury collected on a noble metal such as silver or gold is very simply removed by heating.

SAMPLE HANDLING

To achieve maximum sample handling efficiency, some sort of sampling manifold is required. Various manifolds have been developed to handle measured aliquot volumes or weights of liquid or solid samples and to handle air samples taken in silver absorbers. We have gone through four prototype manifolds and will describe the present one, MCM-4.

Certain basic considerations were used in the design of the manifold.

1. Minimal Requirements:
   (a) Dead volume
   (b) Number of joints
   (c) Number of 90° bends
   (d) Distance from reaction vessel to measuring cell.

2. Applicable to:

   (a) Solid samples such as ground minerals

   (b) Liquid samples such as water or acid digests

   (c) Airborne mercury trapped on noble metal.

3. General Considerations:

   (a) No mercury to be liberated to work place

   (b) Provision for pyrolysis of samples

   (c) Provision for non-recirculating mode

   (d) Provision for recirculating mode, see above

   (e) All necessary fail-safe features

   (f) To be operable by suction

   (g) To be operable by pressure, see above.

The manifolds, so far constructed, are hybrid with respect to materials. MCM-4 contains polyethylene, borosilicate and polytetrafluoroethylene tubing connectors and valves. It is planned to construct ultimately a manifold of stainless steel and a manifold of quartz. It would then be possible to assist the purging of the system with heat by using a bivalve shaped lehr or by means of a flame. A diagram of a non-recirculating manifold for liquid samples is shown in Fig. 1. A diagram for a non-recirculating manifold for solid samples is shown in Fig. 2. The operation of this second manifold will be briefly described.

In order to measure mercury levels in the laboratory, some sort of zero adjustment is required. This may be done by purging with "clean" nitrogen or "clean" air. Clean in this instance means "mercury free". As might be expected, it is found that nitrogen and air supplies cannot be used as "zero" gases without prior removal

of the mercury impurity which is normally present.

MANIFOLD OPERATION

Nitrogen Channels

1. To zero the instrument, using nitrogen, valves A, B, C, D, E, F and G are connected in series. The nitrogen stream is introduced from cylinder 1 through the pressure regulator 2, through back suction trap 3, permanganate solution 4, drierite dryer 5 and reaction vessel 7b. The mercury vapor liberated by heating 7b and its contents enters absorption cell 12, flow meter 13b and exhausts through charcoal filter 6b which prevents the mercury vapor from getting into the laboratory air. Alternatively, an air sample taken on a silver absorber MCA 5 may be inserted in the manifold in place of 7b, the mercury vapor being desorbed from the silver element by heating.
2. The nitrogen carrier gas may be purified by passage through a charcoal scrubber 6a by means of a by-pass from valve B to scrubber 6a. This path is not illustrated in the diagram.
3. The mercury content of the nitrogen carrier may be measured by means of a direct connection from valves B to valve C, thus by-passing the purifying scrubbers. This is not illustrated on the diagram.

The flow rate of nitrogen is checked by flow meter 13b and adjusted by pressure regulator 2. During operation, valves B and C are used as safety openings to present back pressure or to disconnect nitrogen.

Air Channels

1. The instrument may be zeroed by passing the air supply through permanganate solution, valve B being used as the air inlet.
2. Alternatively, the air may be purified by passage through charcoal scrubber 6a.
3. For continuous monitoring of the air ambient to the instrument, valve C is used as the inlet and the air is sucked through the absorption cell using peristaltic pump 14, at a suitable flow rate indicated by flow meter 13b. In this sequence, valves C, D, E, F, G and H are connected in series.

Standardization of Instrument

1. A measured volume of saturated mercury vapor, at known temperature, is injected by means of gastight syringe 9 through softrubber septum 8 into the gas stream.
2. Mercury vapor may be liberated from a measured quantity of a solid standard by heating in vessel 7b.
3. Mercury vapor may be liberated from known amount of standard mercury solution by chemical reduction. This chemical reduction is carried out in aqueous solution in vessel 7a of Fig. 1.

The gas streams containing the known amount of mercury may be led into the absorption cell directly or, by altering the setting of valve F,

through the magnesium perchlorate dryer, check valve 11a and thence into the absorption cell. By making use of the various options, mercury can be measured in:

(a) Liquids, using Hatch and Ott reduction

(b) Solids, using desorption by heat

(c) Air samples on silver, using desorption by heat

(d) Compressed gases, by continuous monitoring

(e) Ambient air, by continuous monitoring.

It was of interest to see whether there was any significant difference in the operation of the manifolds depending upon whether suction or pressure was used as the motive force. In Table I, the results of 10 suction operated experiments are tabulated. A standard amount of mercury, 9.94 nanograms, was used in each case. This was trapped in the silver absorbers and desorbed in the usual way, with a mean recovery of 98%. Similar experiments were carried out using pressure with a mean recovery of 97% as shown in Table II.

If standardization is to be carried out by the reduction of known amounts of mercury in acid aqueous solution, it is of interest to know whether such dilute standard solutions of mercury are stable. Dilute standard mercury solutions were stored in 5 types of containers and analyzed over an 8 day storage period. The amount of mercury present in the standard solutions had decreased considerably, the low being 11% and the high 55% on a quantity of 10.0 nanograms per ml. taken. This is illustrated in Table III.

As previously indicated, the known amount of mercury required to standardize the measuring instrument can be provided by means of a measured volume of saturated mercury vapor or by means of the reduction of a known quantity of some mercury salt in solution. Fig. 3 shows the comparison of the standardization curves obtained using the two separate techniques. It is to be noted that each graph is straight but there is a great difference in slope. It has to be accepted that the lower sensitivity found by reduction of liquid standards indicates incomplete recovery. It would be easy to accept this incomplete recovery as a satisfactory condition if the recovery were 95%, but it is not. In the literature, this lack of quantitative recovery is not discussed. As nearly as can be deduced from this literature, various workers are obtaining recoveries which range between 10 and 50% of the amount of mercury thought to have been taken. Again, it might be suggested that a 10% recovery could be a satisfactory analytical condition if it were entirely reproducible. Let us grudgingly accept this as valid. What then happens to precision and accuracy if the aqueous mercury standards used are kept for 2 days or longer? Please see Table III again.

Mention is made, in the literature, of the use of acid, neutral and alkaline solutions of potassium permanganate as absorbing solutions for the collection of airborne mercury. Acid permanganate solution was used in one bubbler to collect the same known amount of mercury. After collection, the mercury was reduced and measured. The mean of 10 such collection and recovery experiments indicated 47% of the mercury taken was recovered. See Table IV.

Further sampling and recovery experiments using acid permanganate were carried out, in this case using 2 bubblers in series. Each bubbler contained 100 ml of 10% sulphuric acid, which was 1% potassium permanganate. The mercury content of the two bubblers was measured one and two hours after sampling. Appropriate blanks were subtracted. The standard curve used for calculation was based upon the liberation of mercury vapor by reduction from standard aqueous solutions of mercury and a re-circulating mode was used. Calculations were made as described in the mercury procedure given in the Perkin-Elmer manual. An appreciable amount of the mercury taken was found in the second bubbler in every case. The total mean percent recovery varied from a low of 30% when 2 hours had elapsed after sampling to a high of 73% if only one hour had elapsed.

The collection and recovery experiments using silver absorbers MCA 5, mentioned in APCD-71-8, have been repeated many times. In Table V, 10 collection and recovery experiments were carried out with a single absorber in the sampling train, the mean recovery being 96%.

Table VI shows the results of 6 recovery experiments using 9.94 nanograms of mercury. In each case 2 silver absorbers, MCA 5, were used in series. The mercury content of the two absorbers was not immediately measured as sampled. Instead, by means of heat, the mercury trapped on absorber 1 was driven into absorber 2. The contents of each absorber were now separately analyzed by desorbing into the measuring cell. It is now seen that most of the mercury

taken is to be found in absorber 2. By adding together the total from each absorber, the mean total collection efficiency for two silver absorbers in series is 99% according to this experiment. In Fig. 4, two of the experiments of Table VI are shown in the form of the recorder tracings.

Using 3 silver absorbers in series, 8 experiments using 9.94 nanograms of mercury were performed. Immediately after collection, each of the 3 sets of absorbers were desorbed with heat and the mercury collected was measured. In Table VII, trace amounts of mercury were to be found in only 5 out of 16 of absorbers 2 and 3. The calculated mean total recovery amounted to 99% which was essentially due to absorber No. 1.

NORMAL LEVELS MERCURY IN AIR

To have some confidence in mercury in air levels found in source or ambient air surveys, some data on "baseline" levels is necessary. Using the Casella portable air sampler, silver absorbers and procedure to be described later, mercury was collected at a few indoor and outdoor locations. The result of the "indoor" survey is tabulated in Table VIII, where values, in nanograms per cubic metre, range from 20 to 1500. In a similar survey at outdoor locations mercury ranges from 5 to 20 nanograms per cubic metre. See Table IX. The sampling locations and mean value at each location are given in Table X. The highest values are associated with laboratory operations. Room 214A can be considered as a mercury source since this is the location where the bulk mercury is stored and purified. Measurements of mercury using this procedure are continuing.

INTERLABORATORY COMPARISONS

Over 30 years experience with "round robin" programmes for the evaluation of methods, has clearly demonstrated that as conducted by most groups or organizations, the collaborative test programme is a failure. There are several reasons for this. One is the desire to have a method which can be used by many different analytical groups in the hope of achieving complete "comparability" or "translatability" of results, within an industrial area, within a particular country or internationally. This results in analytical project planning with the emphasis on the number or quantity of collaborating agencies rather than the quality. As a direct result of having a large group of collaborators, it becomes more difficult to coordinate and to obtain final test results, so that a great deal of time is lost trying to expedite the delinquent analytical groups. Until all analytical results are in, no complete assessment can be made. Such round robin programmes can, and do, run to three years without concrete results being obtained.

Another difficulty associated with the massive and non-selective round robin programme is the desire of many laboratories to participate on the basis of prestige rather than competence. This can only lead to difficulties since the spread of the results is such that exclusions have to be made in the data, which is bad science and bad statistics. It would have been better to have been selective at the outset, deliberately biassing the project by selecting, for participation, only laboratories of proven competence

in that area. It should be evident that it is desired to evaluate the method rather than the analyst and that evaluating both simultaneously is not possible.

If round robin testing is being done, mechanically, to fill up gaps in an organization's manual of methods or to compete with another organization which has already published such a method there is a tendency to rush the test programme, or, alternatively, to postpone the test programme by publishing the method as "tentative" with the vague promise that collaborative testing will ultimately be carried out. A danger implicit in this approach is that when the method is finally collaboratively tested it may be obsolete or it may be found that the method does not perform as advertised and that it should be dropped from the books. This is difficult to do, since although "tentative", the method having been printed and widely distributed is accepted as "standard" or "official", etc. Efforts may even be made to keep the inadequate method on the books to avoid having to admit a mistake has been made.

Certain organizations have an interest in actual collaborative testing of a method, whether this be before or after the method is published. Some organizations operate almost completely on an editorial basis. The Intersociety Committee started out with ground rules which declared collaborative testing to be unnecessary. Now, after publishing perhaps 50 tentative methods, they plan to carry out collaborative testing. By contrast, all methods published by the American Conference of Governmental Hygienists (ACGIH) have been

subjected to collaborative testing before publication. One of the authors of this report is the official referee for mercury for the A.C.G.I.H.

Although there are established systems for the construction of a collaborative test programme, these can break down because of the various factors above-mentioned. One official organization which was constituted to plan, supervise and assess such test programmes in the area of water analysis changed their method of data handling after six years of operation making it difficult to relate data accumulated before and after the change.

A recent horrible example of the incompetence of the unselected group is a recent analytical fiasco with the analysis of sulfur dioxide in air by the West-Gaeke method. An earlier example was the gas chromatogrpahic round robin of a 4 component solvent mixture. Even though the name of each component was given to the collaborators the collective results were so bad that the project had to be abandoned.

The preceding discussion may not seem to apply to the sampling and analysis of airborne mercury. It is most relevant however, since to achieve "concurrence", "absolute accuracy", "comparative precision", etc., in the area of mercury analysis, an obvious tactic is to set up a round robin.

This has been done in a limited and most preliminary way, using solid standards of uncertain origin designated only as "L", "M" and "H".

These were analyzed in this laboratory, and at the same time, aliquot portions were distributed to 4 other laboratories. Our analyses were carried out in May 1971, the last collaborator reported on August 1971. In the tabulation of analytical values given in Table XI, it would seem that the best reproducibility (precision) is given by Lab. 1. It is conceivable that the precision of Lab 3 is just as good but there is no evidence for this since only single assays were performed.

Lab 2 analyzed the samples in duplicate. Since, presumably, this lab was dissatisfied with the agreement of the duplicates, a third analysis was carried out on each of the three samples at a later date. By going from duplicate to triplicate, ground was lost on sample "M".

In Table XII, "n" the total number of assays and the overall mean is given for each of the three solid standards. Since "n" varies so widely and since the "n" of Lab 1 is so much larger than the other "ns", the mean values are necessarily weighted towards Lab 1. Please note, however, that such weighting is not the fault of Lab 1 but due to the deficiencies of the other collaborating laboratories, all of whom were advised of the results obtained by Lab 1 and given enough material to carry out 6 assays of each standard.

Accepting these overall mean values as meaningful, we have to throw out the values of Lab 2 for "L" and "M" and the value of Lab 3 for "H".

We have now received 6 standard samples of ground rock from the U.S. Geological survey in generous quantity. These are now being analyzed for mercury. It is hoped to be able to set up a preliminary mercury round robin using these samples as mercury standards but only in collaboration with Labs 4 and 5.

RECOMMENDED SAMPLING PROCEDURES

Among the "personal" air samplers available commercially, that manufactured by Casella of London, England, seemed to have certain advantages. It can be carried in a coat pocket, with some difficulty. It is distributed in Canada by Carleton Instruments, Ottawa, at a unit price of Can. $150.00 and in lots of 10 at $111.50. The pump is driven by a rechargeable nickel cadmium battery. The charged battery is able to drive the motor for 7-12 hours at a sampling rate up to 3000 ml per minute. It has an accurate built-in timing device which gives a cumulative digital read out. There is a built-in flow regulator, which can be checked for accuracy using a "standard" flow meter externally. The diaphragm pump is solidly built and is driven by an ingenious gear transmission. This sampler was found to maintain a constant flow rate with MCA 5 silver absorbers.

Certain modifications to the Casella sampler were made. To measure ambient temperature, a shock proof "Stix-on" thermometer was attached to the outside of the case with silicone glue. The floating plug switch was replaced by a small micro switch with a "normally off" arrangement. By tilting the case 90 degrees and placing the samples on a flat surface, the button is depressed

actuating the motor. This is useful if it is desired to sample for long periods such as 2 hours. Two metal terry clips were installed on the case to hold the absorber in position during sampling. A jack was installed for the plug of the timer. When the timer plug is in the jack the electric current between battery and motor is broken and the timer regulates the intervals. When the battery charger is in place and connected to the mains voltage, the sampler runs without battery drain. Two clock-work timers were acquired and provided with electrical plugs to match the jack in the sampler body. One timer covers the range 0-60 seconds and the other the range 1-60 minutes.

Instead of using the timers, a short-wave receiver can be plugged into the electrical jack. It is then possible, if a group of these sampler-receivers are available, to spot these around a source in a suitable geometrical pattern. Using a modified short-wave walky-talky transmitter, it is possible to start and stop all samplers in a truly simultaneous way so that all samples relate to precisely the same period in time. A drawing of the modified sampler and absorber is shown in Fig. 5.

In general, the first air samples taken in any survey are likely to be off scale either upwards or downwards. If there is some first hand knowledge of what the mercury in air concentrations might be, use may be mde of Tables XIII and XIV for anticipated high and low concentrations of mercury in air. For the first set of samples, if enough samplers are available, it is expedient to run samplers in parallel but taking different volumes of air.

Table XV is an example of a sampling form to be used with the Casella sampler. The conscientious use of such a form in the field will expedite subsequent laboratory analysis.

In Table XVI we have a tabulation of data relating absorbance, nanograms of mercury and temperature. It is to be noted that each experimental figure is the mean of 3 determinations. This basic data can be used to construct nomographs and calibration curves in various appropriate formats.

The analytical value found in a mercury assay will vary depending upon the kind of instrumental display and the units employed. The values obtained by using the Du Pont 400 analyzer are usually presented on a strip chart recorder in arbitrary units which may be converted to nanograms of mercury concentrations, etc. To calculate the mercury levels in whatever system is used, it is useful to have suitable computer programmes worked out in advance. A group of programmes for this purpose are briefly described in Tables XVII, XVIII and XIX, under serial numbers 014 to 022 inclusive.

CONCLUSIONS

The electronic deficiencies of the amplifier used in the Du Pont analyzer have been brought to light with the use of the DVM out-put. Zero drift which is not noticeable on the recorder read-out becomes very evident when the DVM display is used. This suggests at some future date a better amplifier should be designed and constructed, probably in house.

The silver element absorbers continue to be quantitatively reliable both with respect to collection and desorption of the mercury collected. The sensitivity, per determination with the total Du Pont assembly seems to be somewhat better than the 0.3 nanograms of elemental mercury claimed in APCD 71-8. Data, so far unreported, indicates there is little analytical interference from other substances. From the limited analytical data so far accumulated it seems that "background" levels of mercury can be as low as 5 nanograms of mercury per cubic metre.

WORK IN PROGRESS

To take care of possible offscale excursions where the quantity of mercury assayed is over 10 nanograms, experiments are being carried out with an integrating digital voltmeter. This allows us to capture the offscale reading. We are now evaluating the DVM readings to see if linearity is being maintained with these off-scale readings.

A preliminary calibration of the Geomet analyzer has been made by analyzing room air simultaneously by means of the Geomet and the Du Pont. Results are shown in Table XX which is satisfactory as a first approximation. We are still waiting for a shorter cycle timer which is to be supplied by the Geomet company. The present sampling cycle is the minimum possible with the present timer. It amounts to 2 minutes and 40 seconds. The read-out of the Geomet is digital and represents the mean value in arbitrary units taken over the cycle of 2.66 minutes. The company supplies calibration curves which can be used to convert the arbitrary digital units to nanograms

of mercury per cubic metre of air. As opposed to the Scintrex, which is a continuous analyzer, the Geomet is semi-continuous. It is, however, quite likely that we will find it is possible to reduce the sampling cycle to one minute without any trouble with sensitivity.

Other work in progress is presented in abbreviated form below:

3. Silver absorbers being redesigned with larger silver element and larger capacity for mercury.
4. Mercometer is to be evaluated.
5. HM Factory inspectorate sampler to be evaluated.
6. Kruger-Beckman analyzer to be evaluated.
7. Evaluation of PE403 spectrophotometer is continuing.
8. Coleman analyzer to be evaluated.
9. Details of electronically controlled survey being worked out.
10. Evaluation of DVM output from Du Pont is continuing.
11. Evaluate use of silver absorbers for water analysis.
12. Determination vapor pressure mercury compounds is continuing.
13. Survey of mercury levels in air is continuing.

TABLE CAPTIONS

TABLE I

EFFICIENCY SILVER ABSORBERS

Test No	Mercury Liberated ng	% Recovery
1	9.48	95.4
2	9.93	99.9
3	9.92	99.8
4	9.38	94.4
5	9.67	97.3
6	9.93	99.9
7	9.85	99.1
8	9.74	98.0
9	9.80	98.6
10	9.70	97.6
	Mean	98.0
	Standard Deviation	1.9
	S.M.E.	0.6

Recovery of 9.94 nanograms of mercury taken
Gas stream moved by suction

TABLE II

EFFICIENCY SILVER ABSORBERS

Test No	Mercury Liberated ng	% Recovery
1	9.46	95.2
2	9.52	95.2
3	9.30	93.6
4	9.94	100.0
5	9.94	100.0
6	9.32	93.8
7	9.80	98.6
8	9.85	99.1
9	9.67	97.3
10	9.70	97.6
	Mean	97.1
	Standard Deviation	2.4
	S.M.E.	0.76

Recovery of 9.94 nanograms of mercury taken
Gas stream moved by pressure

TABLE III

STABILITY STANDARD MERCURY SOLUTIONS

Nanograms mercury per ml

Bottles	Storage Time, Days				
	0	1	2	3	8
Soft glass	10.0	9.97	8.60	6.90	5.50
Pyrex glass	10.0	8.21	7.40	4.20	3.10
Polyethylene	10.0	10.0	7.40	6.00	1.10
Polypropylene	10.0	10.0	10.0	6.20	3.20
Polypropylene, brown	10.0	4.80	4.60	3.30	2.20

TABLE IV

EFFICIENCY ACID PERMANGANATE

Test No	Mercury Lost ng	Mercury Liberated ng	% Recovery
1	1.4	4.4	45.9
2	0.5	4.7	49.0
3	1.4	4.2	43.8
4	0.8	4.2	43.8
5	1.1	4.1	42.8
6	1.0	4.4	45.9
7	0.7	5.1	53.2
8	0.7	4.6	48.0
9	0.3	4.7	49.0
10	1.0	4.7	49.0
	Mean		47.0
	Standard Deviation		3.2

TABLE V

EFFICIENCY SILVER ABSORBERS

Test No	Mercury Lost ng	Mercury Liberated ng	% Recovery
1	0.1	9.3	93.6
2	0.4	9.5	95.6
3	0.3	9.5	95.6
4	0.2	9.5	95.6
5	0.1	9.5	95.6
6	0.1	9.5	95.6
7	0.5	9.4	94.6
8	0.1	9.6	96.6
9	0.0	9.9	99.6
10	0.0	9.9	99.6
	Mean	9.56	96.2
	Standard Deviation	0.19	1.9

TABLE VI

EFFICIENCY SILVER ABSORBERS

Two Absorbers in Series

Test No	Mercury Liberated No 2	Mercury Liberated No 1	Total % Recovery
1	9.91	0.19	99.7
2	9.94	0.00	100.0
3	9.87	0.12	99.3
4	9.68	0.00	97.4
5	9.94	0.00	100.0
6	9.67	0.12	97.3
	Mean 9.83		99.0
	σ 0.12		1.3

9.94 nanograms mercury injected

TABLE VII

EFFICIENCY SILVER ABSORBERS

Three Absorbers in Series

Nanograms Mercury Trapped

Test No	Absorber 1	Absorber 2	Absorber 3	Total Recovery	% Recovery
1	9.93	0.00	0.00	9.93	99.9
2	9.82	0.10	0.00	9.92	99.8
3	9.85	0.10	0.10	9.95	100.1
4	9.93	0.00	0.00	9.93	99.9
5	9.80	0.00	0.00	9.80	98.6
6	9.82	0.10	0.00	9.92	99.8
7	9.79	0.10	0.00	9.89	99.5
8	9.92	0.00	0.00	9.92	99.8
		Mean 9.86		9.90	99.7

9.94 nanograms mercury injected

TABLE VIII

INDOOR SURVEY

MERCURY IN AIR

Date 1971	Location	Sampling Time Min.	Nanograms Hg/m^3	Mercury ppb
July 5	E	62.9	22.4	0.0027
July 5	E	57.5	67.8	0.0082
July 5	E	49.0	65.7	0.0080
July 5	E	47.7	46.3	0.0056
July 5	E	51.3	41.9	0.0051
July 5	E	57.2	80.0	0.0097
July 5	E	57.1	51.8	0.0063
Aug 6	F	4.9	995.	0.121
Aug 6	F	4.6	815.	0.0994
Aug 6	F	4.8	1172.	0.143
Aug 6	F	4.6	1223.	0.143
Aug 6	F	4.4	1107.	0.135
Aug 6	F	4.7	1093.	0.133
Aug 7	F	3.9	770.	0.0938
Aug 7	F	3.9	690.	0.0841
Aug 7	F	3.8	714.	0.0870
Aug 7	F	3.8	720.	0.0877
Aug 7	F	3.6	515.	0.0628
Aug 7	F	4.1	698.	0.0851
Aug 16	G	85.5	20.7	0.00252
Aug 16	G	85.5	17.3	0.00211
Aug 16	G	85.5	17.8	0.00217
Aug 16	G	85.5	22.7	0.00276
Aug 16	G	85.5	20.7	0.00252
Aug 16	G	85.5	18.5	0.00225
Aug 16	H	65.0	54.7	0.00667
Aug 16	H	65.0	68.6	0.00836
Aug 16	H	65.0	60.0	0.00731
Aug 16	H	65.0	69.5	0.00848
Aug 16	H	65.0	62.8	0.00766
Aug 16	H	65.0	61.8	0.00754
Aug 17	I	66.0	51.6	0.00639
Aug 17	I	64.0	51.9	0.00633
Aug 30	J	2.0	1514.	0.185
Aug 30	J	2.0	1360.	0.166
Aug 30	J	2.0	1521.	0.185
Aug 30	J	2.0	1885.	0.230
Aug 30	J	2.0	1465.	0.179
Aug 30	J	2.0	1498.	0.183
	n		39	39
	mean		531.5	0.0647

TABLE IX

OUTDOOR SURVEY

Mercury in Air

Date 1971	Location	Sampling Time Min.	Nanograms Hg/m^3	Mercury ppb
Aug 16	A	92	5.67	0.00069
Aug 16	A	92	5.39	0.00066
Aug 16	A	92	6.16	0.000751
Aug 16	A	92	4.82	0.000587
Aug 16	A	92	4.04	0.00049
Aug 16	A	92	6.49	0.00079
Aug 17	B	100	4.30	0.00053
Aug 17	B	100	5.29	0.00065
Aug 18	C	97	5.81	0.00078
Aug 18	C	91	6.47	0.00079
Aug 18	C	97	4.23	0.00052
Aug 18	C	97	5.06	0.00062
Aug 18	C	90	5.97	0.00073
Aug 18	C	91	5.84	0.00072
Aug 19	D	61	22.0	0.00268
Aug 19	D	59	27.6	0.00336
Aug 19	D	60	20.8	0.00254
Aug 19	D	63	38.4	0.00468
Aug 19	D	59	46.8	0.00566
Aug 19	D	60	17.4	0.00212
	n		20	20
	mean		12.43	0.00151

TABLE X

SAMPLING LOCATIONS

Code Letters	Location	Mean	n	Date 1971
A-O	Argyle & Bank	5.43	6	Aug 16
B-O	Georgina Drive	4.80	2	Aug 17
C-O	Tunney's Pasture	5.56	6	Aug 18
D-O	Springland Drive	28.8	6	Aug 19
E-I	Room 220	53.7	7	July 5
F-I	Room 228	1067.5	6	Aug 6
F-I	Room 228	684.5	6	Aug 7
G-I	Springland Drive	19.6	6	Aug 16
H-I	Riverside Drive	62.9	6	Aug 16
I-I	Georgina Drive	51.8	2	Aug 17
J-I	Room 214A	1540.0	6	Aug 30

O Outdoors

I Indoors

Mean, ng Hg/m^3

TABLE XI

MERCURY CONTENT SOLID STANDARDS

Nanograms Mercury per Gram

Standard	Lab 1	Lab 4	Lab 2	Lab 3	Lab 5
"L"	33	50	88	54	35
	34	50	83		38
	32	50			38
	33	30			
	31	40	84		
	28				
Mean	31.8	44.0	85.0	54.0	37.0
"M"	135	120	260	128	145
	146	110	260		152
	147	100			140
	142	---			
	163	100	340		
	125				
Mean	143.0	107.5	286.7	128.0	145.7
"H"	366	260	280	223	325
	378	280	440		310
	375	280			335
	357	280			
	353	260	250		
	355				
Mean	364.0	272.0	323.3	223.0	323.3

TABLE XII

MEAN VALUES SOLID STANDARDS

Nanograms Mercury per Gram

Standard	Lab 1	Lab 4	Lab 2	Lab 3	Lab 5	Overall Mean
"L"	31.8	40.4	85.0	54.0	37.0	46.2
n	6	5	3	1	3	18
"M"	143.0	107.5	286.7	128.0	145.7	159.6
n	6	4	3	1	3	17
"H"	364.0	272.0	323.0	223.0	323.3	317.0
n	6	5	3	1	3	18

TABLE XIII

MERCURY COLLECTION AT RANGE 2000 $\mu G/M^3$

Mercury $\mu g/m^3$	Vol. Air max, ml	Collection Time, Seconds	
		1500 ml/min	1000 ml/min
0.025- 0.5	20,000	800	1,200
0.05 - 1	10,000	400	600
0.1 - 2	5,000	200	300
0.25 - 5	2,000	80	120
0.5 - 10	1,000	40	60
1.0 - 20	500	20	30
1.5 - 30	333	13	20
2.0 - 40	250	10	15
2.5 - 50	200	8	12
5.0 - 100	100	4	6
10 - 200	50	*	*
20 - 400	25	*	*
40 - 800	12.5	*	*
50 - 1000	10	*	*
100 - 2000	5	*	*

* By syringe

TABLE XIV

MERCURY COLLECTION AT RANGE 2000 NG/M^3

Mercury Ng/m^3	Vol. Air max. 1	Collection Time, Min	
		1500 ml/min	1000 ml/min
1.0- 20	500	333	500
1.5- 30	333	222	333
2 - 40	250	167	250
2.5- 50	200	133	200
5 - 100	100	67	100
10 - 200	50	33	50
15 - 300	33	22	33
20 - 400	25	17	25
25 - 500	20	13	20
30 - 600	17	11	17
40 - 800	13	8	13
50 - 1000	10	7	10
100 - 2000	5	3	5

TABLE XV

SAMPLING DOCUMENTATION

Serial No Sampler	Absorber No	Temp °C	Casella Timer Start	Casella Timer Stop	Sampling Time Start	Sampling Time Stop	Flow l/min	Vol Litres
15	999	25.0	1234.56	7891.23	23.00	23.05	1.0	90.0
XX	XXX	XX.X	XXXX.XX	XXXX.XX	XX.XX	XX.XX	X.X	XX.X
.								.
.								.
.								.
.								.
.								.
.								.
.								.
XX	XXX	XX.X	XXXX.XX	XXXX.XX	XX.XX	XX.XX	X.X	XX.X
.								.
. . . . .								

TABLE XVI

MERCURY IN NANOGRAMS VS ABSORBANCE

Temp C°	10	8	6	4	2	1.5	1.2	1.0	0.8	0.4
	Absorbance X 10^3									
22.0	37.1	29.3	21.8	14.1	7.9	5.9	4.8	3.9	3.1	1.6
23.0	35.6	29.0	22.0	13.9	7.4	5.5	4.4	3.7	3.0	1.5
24.0	35.1	27.8	21.3	13.8	6.9	5.2	4.1	3.5	2.8	1.4
24.5	35.4	28.5	21.1	14.1	7.0	5.3	4.2	3.5	2.8	1.4
25.0	35.6	28.0	21.2	14.4	6.6	5.1	4.2	3.6	2.7	1.3
26.0	34.2	27.3	21.1	14.1	6.7	5.1	4.0	3.4	2.7	1.3
28.0	33.9	27.4	20.7	13.6	6.7	5.0	4.0	3.2	2.7	1.3
mean	35.3	28.2	21.3	14.0	7.0	5.3	4.2	3.5	2.8	1.4
S.D.	1.1	0.8	0.5	0.3	0.5	0.3	0.3	0.2	0.2	0.1
S.M.E.	0.40	0.29	0.17	0.1	0.18	0.12	0.11	0.08	0.06	0.04

Note: Each figure is mean of 3 determinations

TABLE XVII

OLIVETTI PROGRAMMES

014 Silver absorbers, 400 analyzer

Input: Peak height in arbitrary units
Sampling time in minutes
Flow rate in ml per minute

Print out:
1. Absorbance X 10^3
2. Nanograms mercury
3. Mercury in moles X 10^{12}
4. Volume of air samples, ml
5. Mercury, nanograms/m^3, uncorrected
6. Mercury, nanograms/cubic foot, uncorrected

015 To calculate PUT corrections for any system

Input: Ambient temperature in °C
Ambient pressure in mm mercury
Mercury, nanograms/m^3, uncorrected

Print out:
1. Mercury, nanograms/m^3, at 760 mm Hg and 25°C
2. Mercury, nanograms/cubic foot, at 760 mm Hg and 25°C
3. Mercury ppb in air at 760 mm Hg and 25°C

TABLE XVIII

OLIVETTI PROGRAMMES

016 Temperature Conversion

Input: Temperature in degrees F,C or K

Print out:
1. Degrees F and K from °C
2. Degrees C and K from °F
3. Degrees C and F from °K.

017 To calibrate sampling flow rate of Geomet

Input: Pressure, in mm Hg, inches water or lbs sq inch

Print out:
1. Mm Hg and lbs sq inch from inches of water
2. Inches of water and lbs sq inch from mm Hg
3. Inches of water and mm Hg from lbs sq inch

018 Pressure Conversion

Input: Barometric pressure in inches Hg, mm Hg or millibars

Print out:
1. Mm Hg and millibars from inches Hg
2. Inches Hg and millibars from mm Hg
3. Mm Hg and inches Hg from millibars

TABLE XIX

OLIVETTI PROGRAMMES

019 Using Du Pont 400 Analyzer continuously

Input: Peak height in arbitrary units

Print out:
1. Nanograms mercury per cubic metre, uncorrected
2. Nanograms mercury per cubic foot, uncorrected
3. Mercury in ppb, uncorrected
4. Mercury in ppm, uncorrected

020 For calculation mercury in solid samples

Input: Assumed concentration mercury in ppb or ng/gram

Print out: Optimum sample weight, milligrams, for 1 assay

021 For calculation mercury in solid samples

Input:
Weight dish and sample, milligrams
Weight of dish after sample transfer, milligrams
Peak height in arbitrary units

Print out:
1. Nanograms mercury per sample
2. Nanograms mercury per gram
3. Concentration mercury ppb w/w

022 For Geomet semi-continuous analyzer

Input:
Air flow rate, lpm
Sample collection time in minutes
Nanograms mercury collected by second grid

Print out:
1. Nanograms mercury per cubic metre, uncorrected
2. Nanograms mercury per cubic foot, uncorrected
3. Mercury in air, ppb, uncorrected

TABLE XX

INITIAL CALIBRATION GEOMET

Nanograms mercury per cubic metre

Room	Time	Absorber	Geomet
228	11.00	119.4	111.2
228	et seq	139.3	125.5
228	et seq	99.5	125.5
	Mean	119.4	120.7
228	13.20	89.5	84.4
228	et seq	89.5	102.5
228	et seq	79.6	92.5
	Mean	86.2	93.1

FIGURE CAPTIONS

1. Sample handling manifold for liquids, non-recirculating.

2. Sample handling manifold for solids, non-recirculating.

3. Comparison liquid and vapor standard curves.

4. Collection efficiency two silver absorbers in series.

5. Schematic of modified Casella sampler.

Fig 1

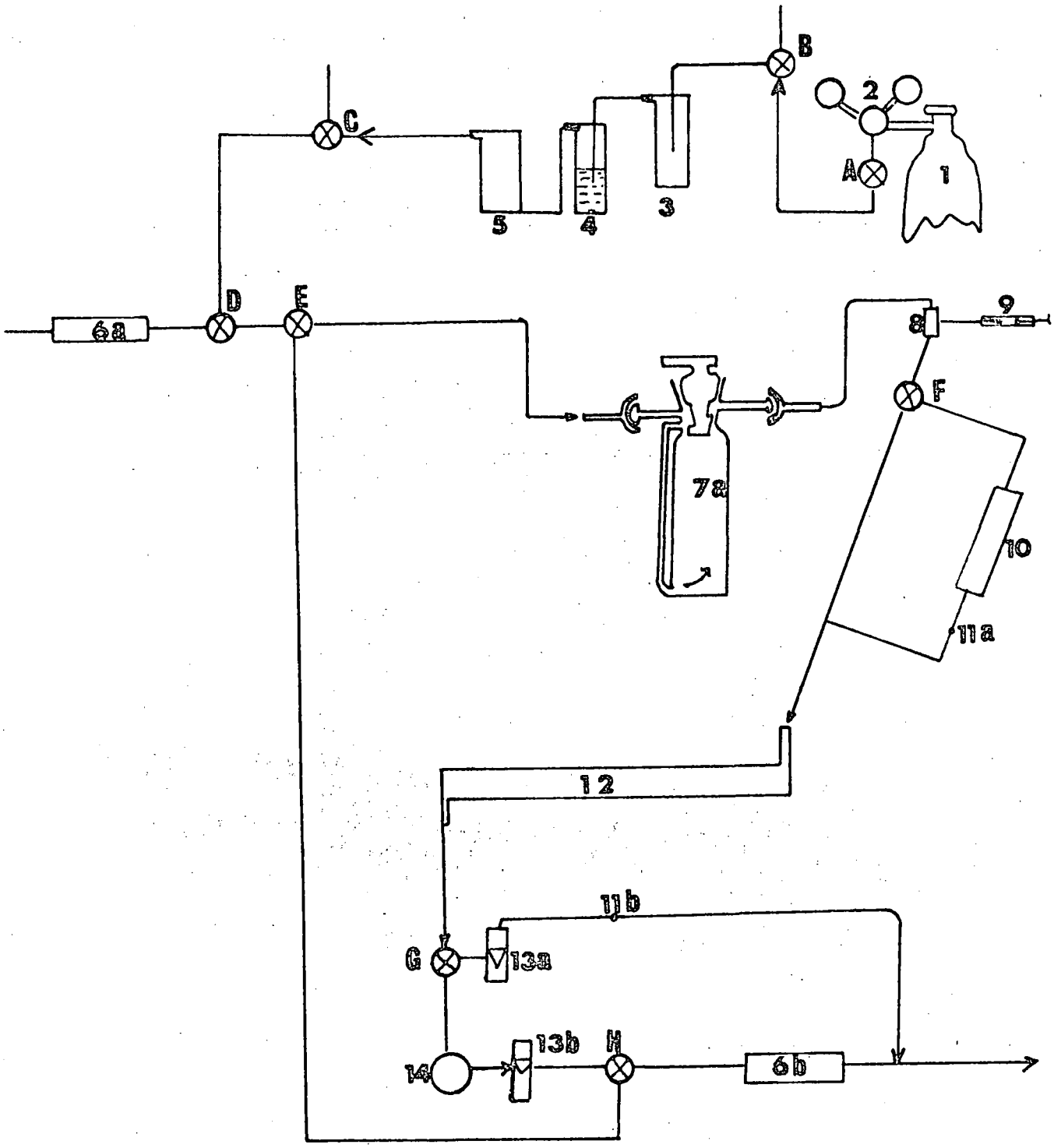
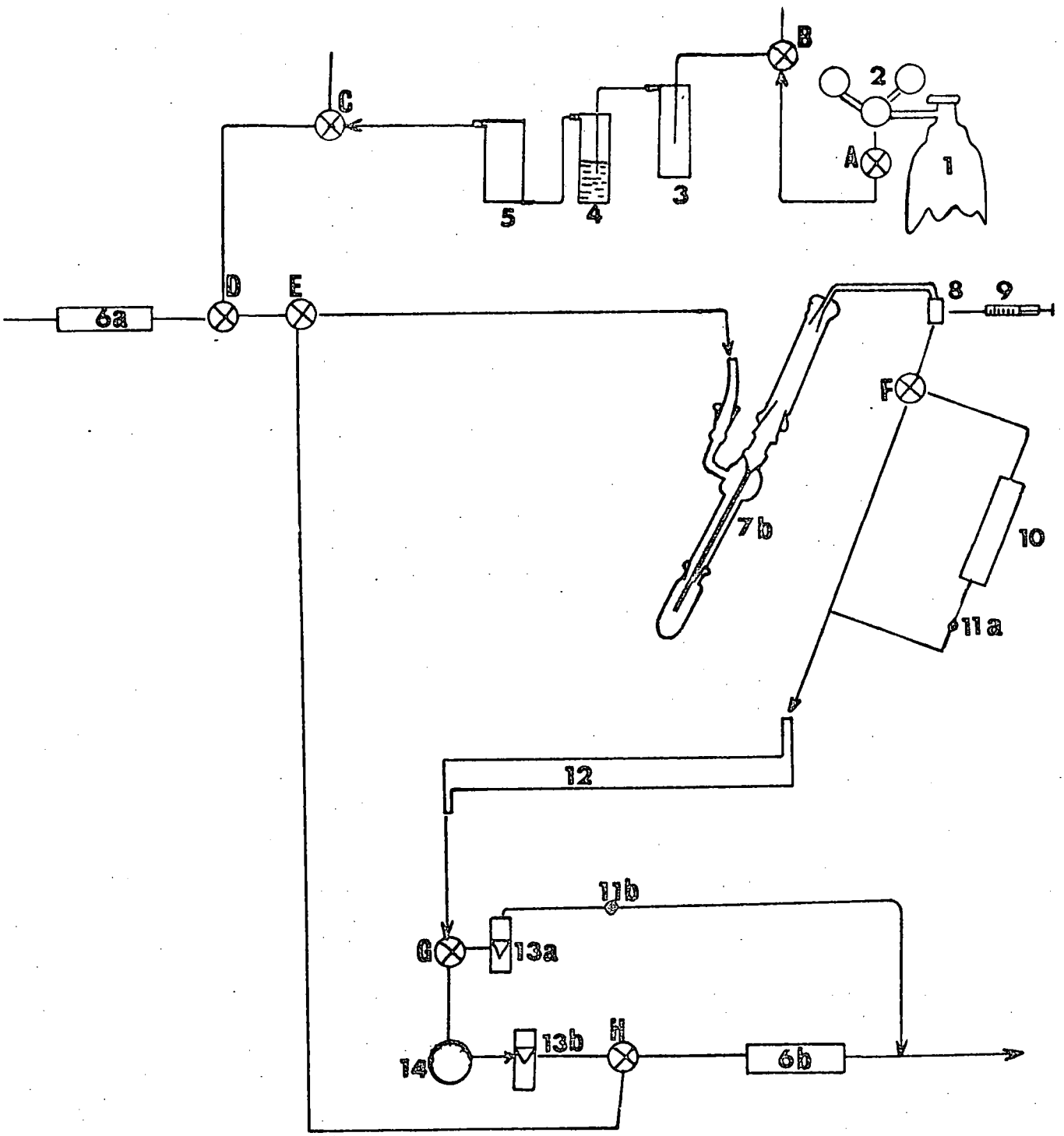


Fig 2



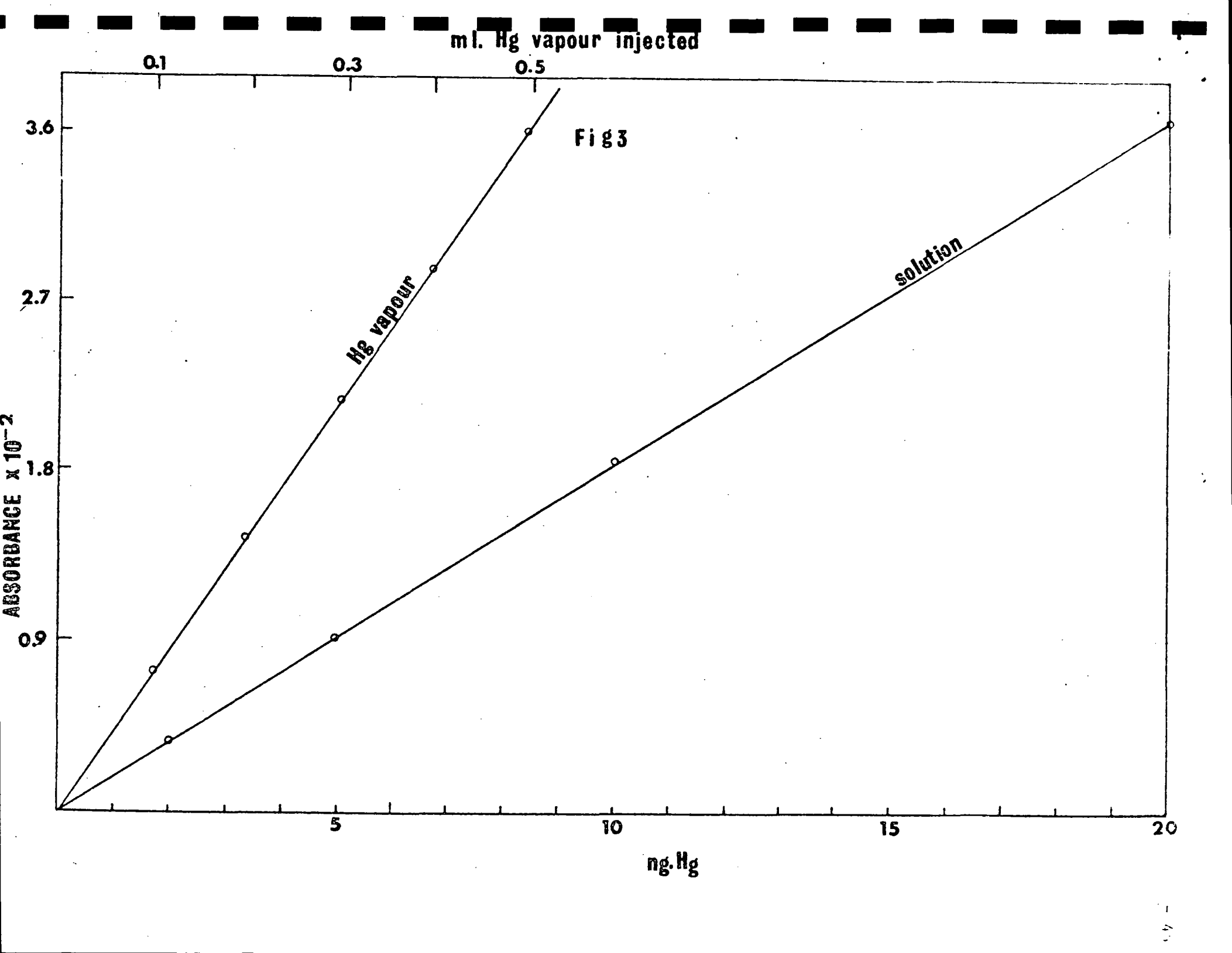
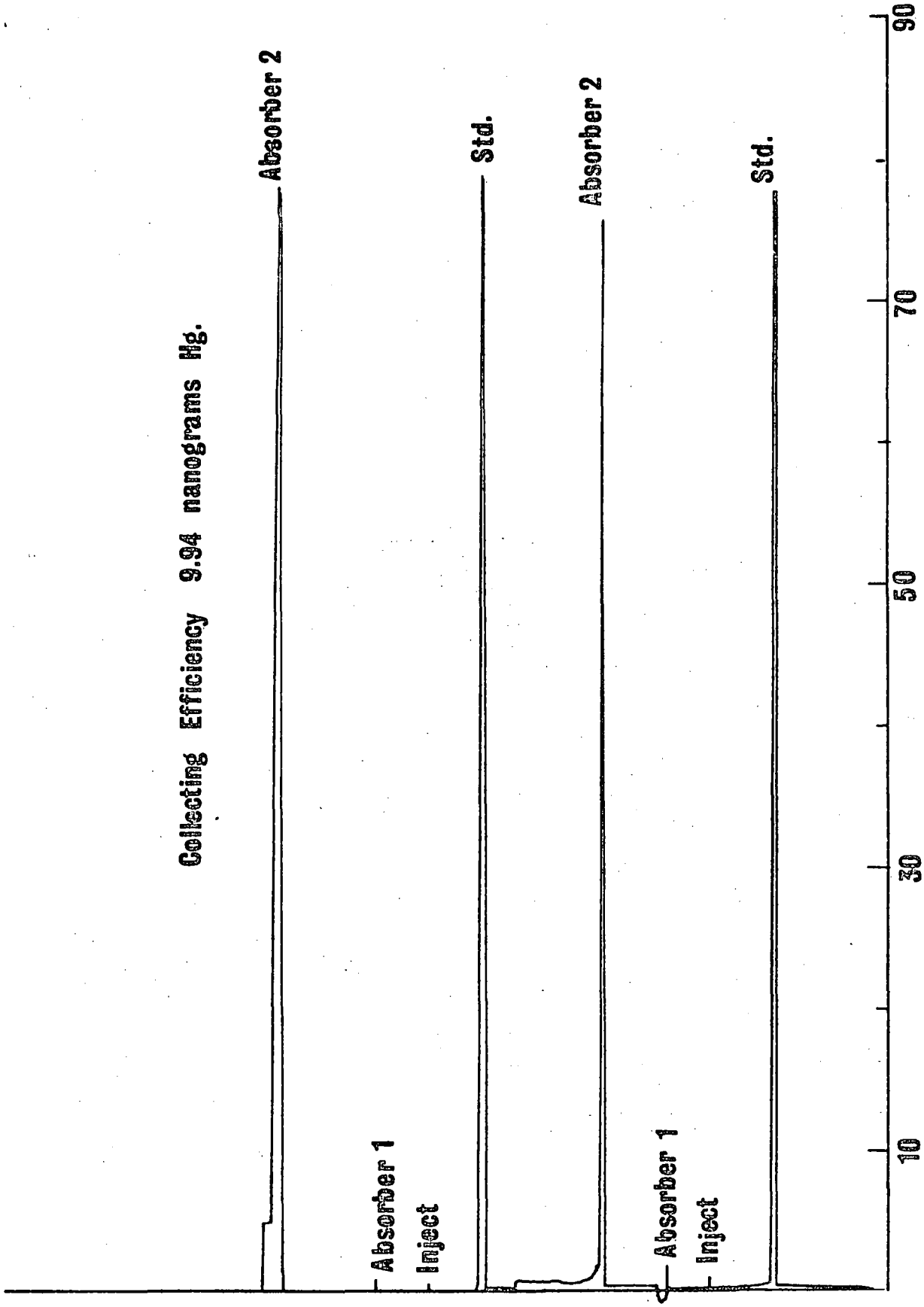

ml. Hg vapour injected
0.1
0.3
0.5
3.6
2.7
1.8
0.9
ABSORBANCE x 10⁻²
Hg vapour
solution
5
10
15
20
ng.Hg

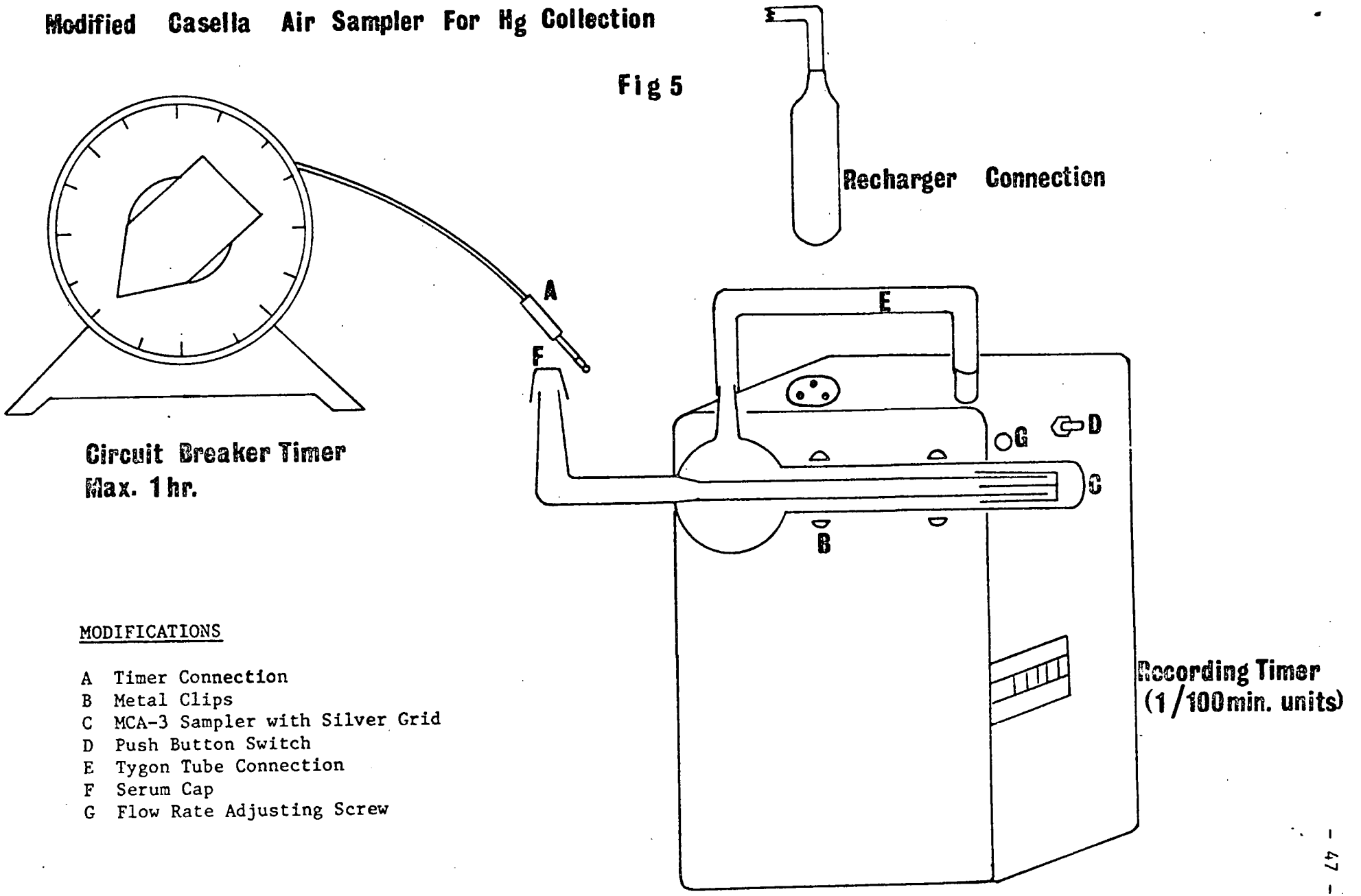
Fig 3

Fig 4


Collecting Efficiency 9.94 nanograms Hg.
Absorber 2
Std.
Absorber 2
Std.
Absorber 1
Inject
Absorber 1
Inject
10
30
50
70
90

Modified Casella Air Sampler For Hg Collection

Fig 5



MODIFICATIONS

A Timer Connection
B Metal Clips
C MCA-3 Sampler with Silver Grid
D Push Button Switch
E Tygon Tube Connection
F Serum Cap
G Flow Rate Adjusting Screw