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THE COLLECTION AND MEASUREMENT OF

AIRBORNE MERCURY. III

APCD 71 - 14

by

G. Corte, R.C. Lao, L. Dubois, R.S. Thomas & J.L. Monkman

Chemistry Division Air Pollution Control Directorate

CANADA

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ABSTRACT

In reports I and II, some preliminary information was provided on the use of silver absorbers in the sampling and analysis of airborne mercury. Collection efficiency, flow rates and sampling devices were considered. Further details are presented at this time.

Considerable effort was spent on the evaluation of portable "personal" air samples. Two separate samplers and absorbers were calibrated beforehand to be as nearly as possible identical i. performance and the sampling time was carefully measured. The two samplers were positioned closely together in order to sample the same air mass. After having performed a sufficiently large number of experiments, it was possible to obtain a statistical rating of the precision of the duplicates. Having this statistical norm it is then possible to introduce an element of quality control into mercury levels determined on such air samples. If the agreement between the duplicates is less than the established norm, this can be used as a criterion for rejecting the analytical values which lie outside this norm.

Preliminary experiments carried out with several organo mercury compounds seem to suggest that it may be possible to sample these materials on silver elements either as the organic vapor or as the mercury component of the compound. Work is in progress to elucidate the nature of the response and to make it quantitative.

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LATION OF LEVEL

This is the third 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 second was APCD 71-2 dated September 17, 1971. In the present report, the preparation of the silver absorbers is described in detail. Also discussed is the collection efficiency and the stability of the collected sample and the fairly large scale use of personal samplers to carry out mercury in air surveys.

SILVER ABSORBERS

Silver gauze, 60 mesh per linear inch, is listed in most chemical supply catalogues as a standard item, in squares 150 mm square. This material contains 99.99% silver, after degreasing, according to the various suppliers. From one square of this silver, measuring 150 x 150 mm, approximately 24 pieces of 33 x 25 mm or 30 pieces 25 x 28 mm can be cut to make 24 mercury silver absorbers. The cost of the silver is about 0.81 per absorber.

The silver gauze is first degreased by washing with acetone, after drying, the gauze is "activated" in a muffle furnace at 850°C for 1 hour. The silver stock may be maintained in good condition indefinitely, if kept in a desiccator over anhydrous calcium sulphate. Experiments were carried out to determine an optimum activation temperature, which was found to be 850°C. The melting temperature of silver is 960°C and experience has indicated that there is no difficulty with heat deformation of the silver elements at 850°C. The activated silver must be handled with clean metal forceps because finger print contamination can produce interfering readings on the ultraviolet analyzer.

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In the course of developing these absorbers a series of variations were constructed as listed in Table I. The quartz absorber (MCA-4) was designed to permit the application of more heat in the desorption process, than can be applied to borosilicate. In addition, quartz has much greater chemical resistance than borosilicate. On account of the greater expense, the quartz absorber has not been evaluated as an air sampling device. A quartz absorber, was however, permanently mounted in the analyzer sampling manifold. The borosilicate absorber MCA-5 has been exhaustively tested and found quite satisfactory. The silver used is 60 mesh gauze purified as previously described. The silver gauze is cut in such a way that it can be rolled into 2 cylinders one inside the other (1). This double cylinder can be fitted in the two concentric glass tubes of the glass envelope so that there is a change in air flow direction part way along the silver element.

Although, as mentioned, silver gauze is listed in the usual chemical catalogues as a stock item, our experience has been that it is merely another fictitious catalogue entry. Orders were placed with all known suppliers but deliveries ranged from 2 to 3 months after receipt of order. The only reason that it was possible to carry out the necessary collection and recovery experiments on schedule, was because a quantity of silver gauze was already on hand within the organization. This was sufficient for the production of the first 100 absorbers.

Due to the desperate supply situation with respect to silver gauze, a quantity of silver foil, apparently more readily available, was obtained and evaluated as an alternative sampling element. The element used was a piece 40 x 40 mm by 0.127 mm in thickness. Recovery experiments carried out with this element were unsatisfactory, in that the

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the element retrined only 7 nanograms of airborne elemental mercury of 10 injected, see fable II. By contrast, the silver gauze absorbers (MCA-5) can trap 100 nanograms of mercury. This is illustrated in Table III. In this table, the readings shown are DVM readings in millivolts obtained by using a Hewlett Packard multifunction meter, 3450A, connected in parallel with the usual recorder readout of the DuPont 400. In this experiment, 5.0 ml of saturated mercury vapor at 25.0°C was injected into the carrier air flowing at 1500 ml per minute. 6 injections were made directly into the analyzer and another 6 injections were made through the absorber. It is evident that 100 nanograms of mercury are absorbed quantitatively when sampled at a flow rate of 1500 ml per minute. In this recovery experiment, it was possible to overcome the limited range of the analyzer with the help of the multifunction meter. In later experiments, a somewhat better readout was obtained by using a Hewlett Packard gas chromatographic integrator.

It is probable that the reason for the comparatively poor collection efficiency of the silver foil is the smaller surface area. As the supply of silver gauze is not yet assured, it is planned to try to increase the surface area to weight ratio of the foil by various mechanical means. Also on order is a supply of gold gauze, which it is proposed to evaluate against silver as a sampling element, when it is received. Of interest, in such an evaluation, is the fact that the desorbing temperature can be much higher than that of silver. It is also hoped that the retention efficiency for mercury may be somewhat better with gold than with silver.

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The latest design of silver absorber, MCA-7, contains 62 more silver gauge than does MCA-5. 100 such absorbers have been prepared, but this latest design has not yet been evaluated. More silver was used in the belief that the total nanogram collection per unit might be increased.

Figure 1 illustrates some recovery experiments carried out with absorbers MCA-5. Such an absorber contains 1.8 grams of silver in the form of 60 mesh gauze (1). Saturated mercury vapor at a temperature of 25.0°C was injected into the analyzer manifold with a carrier flow rate of 1500 ml air per minute. The DuPont 400 analyzer was used to measure the ultraviolet absorption of the injected mercury vapor. In Figure 1, which is a reproduction of a recorder tracing, peak A is the reading of the built in optical calibration unit in arbitrary recorder chart divisions. Peak B represents the reading produced by a single injection of 0.5 ml of saturated mercury vapor equal to 9.94 nanograms of mercury. The rudimentary peaks at C are the collective readings produced by the consecutive injection of 9 consecutive injections of 9.94 nanograms of mercury. A silver absorber was interposed ahead of the analyzer and it is evident that no significant amount of the 90 nanograms escaped the silver collector. Peak D is equivalent to B, being a direct injection of 9.94 nanograms which by-passes the silver absorber. E is the reading produced by the release, with heat, of the total mercury absorbed on the silver. The reading is well off scale. When this experiment was carried out, it was not possible to handle larger more than 10 nanograms of mercury per determination without an off-scale response. Such off-scale responses are no longer a problem since the total peak is now recorded digitally by a Hewlett Packard integrator. This extends the measuring range of the analyzer considerably. The use of this

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incogration system will be described in a subsequent report. By means of the integrating readout it has been confirmed that the MCA-5 absorber actually collects 100 nanograms of mercury quantitatively.

It was of interest to determine whether an air sample, taken on a silver absorber, was retained quantitatively in storage. Table IV shows the storage of 9.94 nanograms of mercury and desorption after varying storage times. The results indicate some loss after 2 days. When time affords, it is planned to investigate exhaustively this apparent loss with time of storage. Compared with the losses encountered by sampling in permanganate, these losses are insignificant (2) but it is hoped to reduce or elucidate these losses, in future work. It may be that the mercury is not lost, but has merely migrated more deeply into the silver, and that heating nearly to melting might recover this "loss".

It was of interest also to see whether silver absorbers "activated" to be mercury-free remained mercury free in storage. The results of experiments carried out over a total storage period of 14 days are summarized in Table V. Results are not particularly conclusive and suggested that the experiment be repeated again in a more carefully controlled way. There is a slight suggestion of mercury contamination perhaps due to the Tygon tubing used to seal the absorbers prior to use.

INTERFERENCES

Since most mercury analyzers are based upon the absorption by mercury of light of a characteristic mercury line wavelength such as 2537 A°, one might expect the response to be affected by the presence

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of other cluraviolec absorbing vapors. If, for example, one were to make use of the DuPont 400 analyzer to mensure mercury in air, organic vapors such as benzene or toluene would have to be absent. In Figure 8 of Report No. I the response of the 400 analyzer to benzene vapor is illustrated. Also illustrated is the fact that benzene vapor is not retained or collected by the silver absorber. Experiments to assess the possible interference of organic vapor were carried out by measuring the effect of various organic vapors injected directly into the analyzer or injected into the analyzer by way of a silver absorber. Table VI summarizes experiments with acetone, ethyl acetate, dioxane, pyridine and ethanethiol. None of the organic vapors are retained by silver absorber, with the exception of a slight effect when 0.1 ml of pyridine vapor is used.

In Table VII the effects of the organic vapors listed in Table VI are tabulated together with benzene, toluene and para-xylene. Measured amounts were injected directly into the analyzer and the interfering effect was calculated to apparent nanograms of mercury. The interferences are tabulated in decreasing order of effect. Thus to get an effect equivalent to 1 nanogram of mercury, 1.47 nanograms of pyridine would have to be present in the absorption cell. These interfering effects are not important, however, if sampling and analyzing of mercury is based upon the use of a silver absorber to capture the mercury since the organic vapors tested so far are not retained by the silver element.

Certain mercury in air levels have been reported based upon air samples which have been taken on conventional glass high volume or millipore filters. The investigators who did this work were subconsciously assuming several things:

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 That the Browny was quantitatively collected from the air by the subpring method used.

2. That the mercury collected was in particulate form. In spite of the fundamental and well known volatility of mercury and mercury compounds, no work has been reported in the air pollution literature to indicate what the sampling efficiency of any sampling methods or media might have been.

As, in the case of chloralkali plants, airborne mercury is almost certainly volatile elemental mercury and not particulate, there seems little reason to sample elemental mercury by air filtration based upon such things as mechanical adhesion and filter pore size. With these considerations in mind, an investigation was made of an air sample on filter S-74. This Hi Vol sample had been exhaustively investigated previously with respect to airborne sulphate and sulphuric acid (3, 4).

Sample area aliquots of 1 square inch in size were cut with clean scissors and folded with clean surgical forceps into small pellets to fit the reaction vessel. The folded samples were inserted in the heating chamber and heated until the glass fibres melted. The gases evolved, including organic thermal decomposition products, were drawn through an MCA-5 silver absorber, with air as carrier gas, into the measuring cell of the DuPont 400 analyzer. This preliminary separation permitted the registration of the organic ultraviolet impurities, other than mercury. Subsequently and separately, the MCA-5 absorber was heated and the desorbed mercury was measured in the same way. All readings were calculated and expressed as total nanograms of mercury or equivalent per square inch of fibre glass filter. In this experiment, 6 assays were

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carried out on plack fibre glass shoet variety Gelman A water washed. At the same time, 6 assays were carried out on 1-inch square area aliquots of filter S-74. The results are shown in Table VIII, where it may be seen that the amount of mercury present as a blank in a marked unexposed filter is the same as that.present in similar area aliquots of exposed filter. This suggests, for this single experiment and air sample, that no airborne mercury either particulate or volatile had been captured by the air sampling process. It also suggests that the mercury found may be a blank value which is internal and part of the glass fibre structure. It is improbable that mechanically adhering surface mercury contamination could remain after the washing process to which all the filters are subjected.

The fact that some organic ultraviolet absorbing impurity, not mercury, is present in a washed glass fibre blank is consistent with our experience that the so called "flash firing" process does not actually remove all organic material and that it may, in fact, remove very little. The comparatively much higher values for the ultraviolet non-mercury component in the air sample is to be attributed, in all probability, to the sublimation of polycyclic hydrocarbons (5).

ORGANOMERCURIALS

In view of the large quantity of mercury slimicides which have been used in paper manufacture in the past and the ultimate disposal of a large proportion of pulp and paper products by incineration, it is to be expected that any mercury compounds retained by the pulp structure will be liberated to the air. One might expect that phenylmercuric acetate (PMA) and methylmercuric acetate (MMA) liberated in aqueous

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effluents would be in the original organomercurial form as they were added to the manufacturing process. These compounds when incinerated may be broken down to elemental mercury or mercury oxides. There are, however, no experimental facts to prove that these compounds are or are not broken down during incineration.

A number of organomercurial compounds were obtained to evaluate sampling and analytical techniques. These included, among others, dimethyl- and diethylmercury which were investigated by mass spectrometry as previously reported (6). Other compounds on the investigation inventory were as listed in Table IX. It was of interest to see whether these compounds, in the pure state, had a sufficiently high vapor pressure to produce measurable concentrations in air, whether such concentrations could be measured by ultraviolet absorption or whether, indeed, these materials in the vapor or airborne state could be sampled and retained by the silver absorber.

Some experiments were carried out using the Geomet 103-2 semicontinuous sampler and analyzer. In Figure 2 the lower tracing (A) indicates the uniformity of mercury in air concentrations which it is possible to obtain with this analyzer when the mercury is homogeneously distributed within the room. The upper tracing (B), indicates that under other conditions the concentration of mercury in an enclosed area can be guite variable.

Using the Geomet 103-2 semi-continuous sampler and a gold plated sampling element, an open bottle of reagent grade methylmercuric hydroxide was placed before the sampling opening. The qualitative response obtained is illustrated by Figure 3 where there is a sudden rise of the DVM

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reading from of to 483 within the 2 minute sampling cycle of the instrument. With time, there is a gradual decrease of the net DVM readings. The reading after 25 minutes, however, is still 323 as compared with the threshold value of 85. With the removal of the open bottle from the sampling port, the readings return to the threshold level. This experiment suggests that there is some vapor phase material emanating from the bottle which is sampled and measured as metallic mercury. It is possible, of course, that methyl mercuric hydroxide, in the form of vapor, is actually retained by the gold sampling elements of the Geomet.

Similar experiments were carried out on several organomercury compounds and the two oxides of mercury, black mercurous oxide (Hg₂O) and red mercuric oxide (HgO). In this case a Scintrex analyzer was used to monitor the concentrations of vapor above the solid reagent. The Scintrex analyzer is a continuously direct reading instrument. The reagent bottle was opened, covered with lens tissue to prevent the egress of particulate mercury compounds and the bottle was maintained beside the sampling port of the Scintrex until the peak response was obtained. When this occurred and the pen was returning to the baseline, the reagent was removed. Six mercury compounds were evaluated in this way as well as a bottle of rubber cement. The Scintrex has two channels which are recorded separately with a 2 pen strip chart recorder set at a range of 10 volts. The one channel is designed to be specific for mercury, the other channel gives a reading of ultraviolet absorption. In Figure 4 the ultraviolet response is shown by the dashed line and the mercury response by the solid line.

Several things are evident from this crude experiment, such as the proportionately greater response of mercurous over mercuric in the case of the oxides and the much greater response of phenylmercuric- over methylmercuric-. Remembering that the recorder sensitivity is particularly low,

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it is of interest that there appears to be a mercury response from the rubber coment. It is also interesting that the ultraviolet responses are insignificant except for mercurous oxide and the rubber cement. It is not too difficult to imagine the increase in response which would result if the recorder were set at the more usual 1 or 10 mV instead of 10 volts.

The Scintrex response is based upon direct and continuous ultraviolet measurement of the air stream passing through the measuring cell. No precious metal sampling element is employed. Using the DuPont 400 analyzer as the measuring device, measured volumes of the vapor-air mixture over methylmercuric acetate (MMA) were withdrawn by syringe through a serum cap which had been substituted for the normal bottle cap. Six replicate quantities of the vapor were injected directly into the analyzer with the results given by the 6 peaks designated under A on Figure 5. Three similar volumes of the vapor were passed through silver absorbers before entering the analyzer. The position indicated as "B" are where the peaks would have appeared if the material had not been absorbed by the silver elements. Evidently, the ultraviolet absorbing vapor is quantitatively trapped by the silver. The mercury or mercury compounds were now desorbed from the three silver absorbers in the usual way and the desorbed vapor measured by the DuPont 400. The responses are shown as peaks C of Figure 5. It is interesting to note that the apparent mercury response is significantly increased after trapping the "organomercurial" vapor and subsequently desorbing the absorbed species.

The experiment of Figure 5 was repeated using phenylmercuric acetate as the test material. For identical replicate volumes of the PMA vapor injected, it is to be noted in Figure 6 that reproducible readings

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are obtained for direct replicate injections of the vapor, that the vapor is quantitatively trapped by silver and that, as shown by peaks C, the increase in the amount of "mercury" desorbed, is proportionately much greater than is the case with MMA in Figure 5. The increase in response can only be described as tremendous. This data for Figures 5 and 6 is given in tabular form in Table X, where the response is given as absorbance $X \ 10^3$.

AIR SAMPLING AND ANALYSIS

The MCA-5 absorbers are heat activated and both side arms are sealed by means of a 17 mm piece of polyvinyl chloride tubing, Tygon 3603. Suitable dimensions of such tubing are 3/16" ID, 5/16" OD and 1/16" wall thickness. The absorbers are packed individually in polyethylene bags with a sealed in air cushion to diminish possible breakage in shipment. The activation date of the absorber is stamped on a label on the bags. The absorbers remain active for at least 10 days, but experience has shown that they can be safely used up to 20 days after activation. The absorbers should be handled carefully to prevent breakage and contamination by smoke, organics or mercury compounds. The absorbers are easily mounted horizontally in the two terry clips. The short length of tygon tubing is used to make the connection from the inner tube of the absorber to the air intake of the "personal" sampler. In operation, both side arms point downward, to prevent the possible entry of dustfall. After the designated air volume has been drawn, the exposed absorbers are sealed again and packed in polyethylene bags for return shipment to the laboratory. It is recommended that the absorbers should not be delayed longer than 3 days in transit door to door.

The Casella 'personal' sampler, briefly described in APCD 71-12

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(d), be a indecated by evaluated and found to be quite satisfactory for the sampling of elemental mercury in ambient air or the air of the work place. The sampler has a diaphragm pump, driven by a constant speed direct current motor, which operates on a single 4.8 volt nickel cadmium battery. The pump can be operated satisfactorily, with or without interruption, up to a total sampling time of 6 hours. This is based upon the use of an MCA-5 absorber and a completely charged battery. The pump and battery are housed together in a white plastic case. A digital counting indicator shows the elapsed sampling time in minutes. The figures are visible through a window in the side of the housing. A screw adjustment allows an air flow rate setting of 500-3000 ml of air per minute, which can be determined by the use of an external calibrating flow meter.

The sampler can be put into operation in several ways as will be tabulated below.

- (a) For continuous operation, or for complete discharge of the battery, insert the electrical plug into the matching receptacle on the top of the case
- (b) For continuous operation, tilt the case 90 degrees and place the sampler on its side or a flat surface. The pushbutton operated microswitch activates the pump and this is useful when the air samples are to be taken for a longer period than 1 hour
- (c) For timer operation, insert the timer plug into the matching jack installed on the side of the case; the timer now regulates the sampling interval. Two standard clockwork timers have been modified for this purpose,

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one the range of 0-60 seconds and the other for the range of 0-60 minutes.

(d) For remote control operation. The electrical plug of the radio receiver is inserted into the timer jack of the Casella sampler. Several receiver-sampler assemblies can be set up in this way. The sampler or samplers can now be started and stopped simultaneously by signal from the radio transmitter.

Before use of a personal sampler, it must be properly calibrated with respect to flow rate. Before starting the pump of the personal sampler, the inlet arm of the MCA-5 absorber is connected by means of the tygon tube to the rotameter. When the pump is operating, the flow rate is adjusted to the desired rate by means of the screw adjustment. A sampling rate which has been found generally acceptable is 1500 ml per minute. The personal sampler is now ready to sample air at the designated flow rate using a properly charged battery.

The battery charger provided, operates on 110 volts 60 Hz with the usual line operated power cord. Connection to the battery is made by means of the 3 connector socket on the side of the sampler case. If several batteries need to be recharged at the same time and only one 110 volt receptacle is available, the line may be connected to the first charger, after which "OUT" of charger one is connected to "IN" of charger two etc. With the main switch of the charger in the "ON" position a red light indicates that the line is connected, but not that direct current is being provided. Within the charger, the input is adjusted to 110 volts 60 Hz. The output is set at 5.0 volts DC. The indicated output of 5 volts refers

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to the volte of the nickel cadmium battery and not to the open current voltage which is actually 25 volts DC. At the fixed setting described, the charging rate is 90 mA on the 14 and 21 mA on the 64 setting of the charging rate switch. The capacity of the battery is 900 milliampere hours. The discharging rate of the battery using MCA-5 absorbers was measured with an ammeter and found to be 275 mA for samplers 2 and 3 and 210 mA for samplers 4 to 12.

As it is essential that only properly charged batteries be used for sampling, books must be kepton the number of minutes or hours that a battery has been used in sampling. If for example a sampler has been operated for 4 hours, one may wish to recharge at setting 14 according to the formula below:

 $\frac{D}{C} \times TD \times 1.4 = TC \text{ where } D \text{ is discharge rate, mA}$ TD is discharge time, hours C is charging rate, mA TC is charging time, hours

Example:

Unit No. 5 ran for 4 hours. It is to be recharged at setting 14 which is a charging rate of 90 mA. The discharging rate, D, was 210 mA, the discharge time, TD, was 4 hours.

 $\frac{210}{90}$ X 4 X 1.4 = TC = 13.1 hours

If the air sampler has been operated for 4 hours, it may be appropriate to replace it with a sampler which contains a freshly charged battery. The sampler which has been discharged for 4 hours may now be discharged and then recharged overnight at the 14 setting.

According to the manufacturer, repeated overcharging of the battery is to be avoided because it is said to shorten battery life. These

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batteries are the reported to lose power if allowed to stand unused for more than 5 weeks. Therefore, it is recommended that batteries be discharged and recharged immediately before use. Obviously, it is also necessary to keep books on the length of storage time between consecutive uses of such samplers.

In the second report in this series, some reference was made to the sampling of mercury in air using the combination of the silver element and portable battery operated air samplers. In tables XIII and XIV of the previous report APCD 71-12 recommended sampling times are suggested for varying concentrations of mercury in air. The overall sensitivity of the sampling and analyzers is such that very short sampling times are possible when the ambient air concentrations are affected by neighborhood sources.

The evaluation of three portable "personal" samplers was carried out by sampling the laboratory air on silver elements. The three samplers were operated simultaneously adjacent to one another. Before use, each of the samplers was carefully calibrated to operate at identical flow rates. Four experiments were carried out as shown in Table XI. One of the samplers was manufactured by Casella and the other two by Unico, so that equipment from two makers was evaluated. It is evident that the calibrations of the three samplers must be very similar to permit such close agreement in the mercury values found.

Using only Casella equipment, air sampling experiments were carried out in duplicate indoors. Tables XII, XIII, XIV, and XVI give the results of such duplicate sampling experiments. In Tables XII, XIII and XIV every effort was made to have the timing of the duplicate samplings truly identical with respect to starting and stopping the samplers together and with respect to the accuracy of the sampling time interval. It was thought that the

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tiving overation might be improved by the use of simultaneous control of the sampling time period for both samplers by transmitting the start-stop signal by radio signal to receivers operating the Casella samplers. This was done in the experiments of Table XVI. Statistical evaluation of the agreement of the duplicates suggests that, for this experiment, the precision \cdot of the duplicates was not improved by the use of the radio signal. Sampling in triplicate was carried out on October 28, 1971 for a total of 18 triplicate determinations on outside air. As was to be expected, the spread of the triplicate results is greater than for the duplicates.

There are several reasons for taking air samples in duplicate. One reason might be that if the results of one sample are lost in sampling or analysis a matching result may be available. The most cogent reason, of course, is to build in complete quality control of the survey with respect to both sampling and analysis. It is ordinarily much easier to put values on the analytical accuracy and precision than on the overall accuracy of the values which have to be reported. In the case of the sampling and analysis of mercury this problem may be considered solved by the use of the duplicate sampling technique, which includes a data base on the flow ratetime-volume relationship. If, on analysis, the mercury values found for duplicate samplings do not fall within the already established limits there are good grounds for rejection of these values.

As a general operating rule, air samples are to be taken always with two separate but equal samplers which operate simultaneously. The two samplers must be positioned side by side with the inlet openings of the absorbers oriented in parallel. It is not sufficient, nor acceptable, to take two air samples consecutively in time using the same samples. Nor is it acceptable to take simultaneous air samples with the samplers widely separated in space.

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These contra nucleations are specified, at this time, because these sampling errors have already been made in the field with results which confirmed the unacceptability of the results so obtained. A recommended field operational procedure is presented herewith.

- Read the digital value of the time counter and enter on the data sheet
- 2. Enter the serial number of the absorber on the data sheet
- 3. Start the air sampler as previously described
- 4. Adjust flow rate with external rotameter to flow rate chosen, enter flow rate
- 5. When sampling is completed enter time from digital counter
- 6. Seal openings and wrap exposed absorbers for shipment or transit.

WORK IN PROGRESS

The impression is widely current that mercury and mercury compounds in the biological environment are being continuously converted to dimethyl mercury which as a metal-organic compound with high volatility should be just as continuously entering the ambient air environment. If this is so, it is of some importance to be able to sample and measure, or to directly measure, the dimethyl mercury in air. From mass spectroscopic investigations already carried out, in this laboratory, the mass spectral data for dimethyl mercury and diethyl mercury have been established (6). It should be possible, then, by a combination of gas chromatography and mass spectrometry to measure dimethyl mercury as such in the air.

If as is also possible, the residence time of dimethyl mercury in air is ephemeral, the mercury component will undoubtedly remain and be sampled and analyzed by the techniques already described. It may ultimately prove of the gaan passing interest to set up a GC-MS field sampling unit as a point of interest such as the St. Clair River to confirm or otherwise that dimethyl mercury is actually evolving from the biological and aqueous environments.

In view of the need for a sufficient data compilation of the mercury levels now existing in ambient air, sampling surveys are under way to establish such levels with and without the contribution of specifc sources and taking into account the time of year. A double duplicate sampling survey of Ottawa air will be completed on December 25, 1971.

With respect to the possible existence of airborne particulate mercury in air a quantitative method of sampling is required. It is probable that particulate mercury compounds can be quantitatively sampled in precious metal elements and experiments to verify this are planned. The actual vapor pressures and decomposition temperatures of important organo mercury compounds are being investigated by mass spectrometry, differential thermal analysis and thermo-gravimetric analysis. Such physical and chemical data is needed in connection with the development of quantitative sampling methods. Preliminary experiments reported here support the opinion, that for reasons of high vapor pressure, mercury compounds are not retained by high volume air filters.

Since the performance of the DuPont 400 analyzer is limited by the performance of the amplifier, a satisfactory amplifier will be designed and constructed to improve the performance of this analyzer.

CONCLUSIONS

Extensive experiments in the duplicate sampling and analysis of airborne mercury using silver elements allow us to recommend this

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technicse is the fundamental field method for mercury.

For probably the first time in such a field method, a degree of quality control has been built into the sampling and analytical routine which will be of great help to the director of any mercury in air survey.

As well as being a simple method and easily performed, the silver absorber method is of value in the field as a calibration or reference method against which the response of semi-continuous or continuous instruments such as the Geomet or Scintrex can be assessed.

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LIST OF TABLE CAPTIONS

Varieties of silver absorbers to date. I Recovery of mercury by silver foil. II Recovery of 100 nanograms mercury vapor. III Storage and recovery of 9.94 nanograms mercury. IV Mercury blanks of activated silver absorbers in storage. V Ultraviolet interference of various organic vapors. VI Comparative ratings of organic interferences. VII Measurement of mercury in high volume glass filters. VIII Physical properties certain mercury compounds. IX Organomercurials sampled on and desorbed from silver. Х Comparative performance three separate air samplers. XI Duplicate air sampling and measurement, November 4. XII Duplicate air sampling and measurement, November 5. XIII Duplicate air sampling and measurement, November 8. XIV Duplicate air sampling and measurement, October 28. XV Duplicate air sampling and measurement, November 15. XVI

TABLE I

SILVER ABSORBERS

MCA-1	2 separate pieces silver on pyrex
MCA-2	1 piece of silver gauze in pyrex
MCA-3	Same as MCA 2, but custom made
MCA-4	Same as MCA 3, but custom made of quartz
MCA-5	Same as MCA 3, pyrex with longer side arms
MCA-6	Same as MCA 5, using foil instead of gauze
MCA-7	Same as MCA 5 with 6% more gauze

TABLE	II

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RECOVERY OF MERCURY BY FOIL

Assay	Mercury Liberated	Percent <u>Retained</u>
1	7.31	73.4
2	7.33	73.6
3	7.42	74.5
4	7.33	73.6
5	7.36	73.9
6	7.40	74.3

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TABLE III

RECOVERY OF 100 NANOGRAMS MERCURY

Assay	Direct	Through MCA	5 Absorbers
No.	Injection	Hg Escaping	Hg Liberated
1	29.6		
2	28.8		
3	31.2		
4	31.5		
5	30.3		
6	29.8		
7	يت فله که که	0.3	29.3
8		0.6	30.0
9.		0.2	29.7
10		0.3	· 29.1
11		0.4	29.5
12		0.2	29.3
	:		
Mean	30.2		29.5

DVM readings X 8

TABLE IV

STORAGE OF COLLECTED MERCURY

Nanograms after storage

<u>Test No.</u>	Storage	<u>1 day</u>	2 days	<u>3 days</u>
1	9.98	9.71	9.72	9.47
2	9.96	10.00	9.81	9.12
3	9.95	9.72	9.96	9.22
4	9.96	9.90	9.86	9.50
5	9.95	9.83	9.37	9.50
6	9.90	9.84	9.90	8.86
			· ·	
Mean	9.96	9.84	9.71	9.28
± SD	0.1	0.11	0.21	0.26
Recovery %	100.0	98.80	97.49	93.17

TABLE V

SILVER ABSORBER BLANKS

Storage, Days	Absorber <u>No</u>	Peak <u>Height</u>	Mean	S.D. _ <u>+</u>	<u>S.M.E.</u>	Ng Hg
	•					
2	002	0.0				0.000
	005	0.0				0.000
	007	0.5				0.064
	008	0.0			• .	0.000
	009	3.0				0.380
	011	0.0	0.58	1.20	0.49	0.000
4	024	1.5				0.190
•	026	0.5				0.064
	027	0.0				0.000
	028	1.0				0.130
	029	1.0			·	0.130
	030	3.0	1.20	1.03	0.42	0.380
8	041	2.2			· · ·	0.280
-	042	0.5				0.064
	045	0.5				0.064
	048	1.5				0.190
	052	2.0				0.260
	060	0.5	1.20	0.80	0.33	0.064
10	041	0.0				0.000
	042	0.0				0.000
	043	0.0				0.000
	044	0.8			• .	0.100
	045	2.0				0.260
	046	0.5	0.55	0.78	0.32	0.064
14	048	3.5				0.450
	049	3.0				0.380
	052	0.0				0.000
	053	0.5				0.064
	054	0.0				0.000
	056	0.0	1.20	1.60	0.67	0.000

Absorbers MCA 5 sealed with tygon

TABLE VI

INTER PRODUCTIS

Absorbinge 107

Test <u>No</u>	Direct to Cell	Through Sampler	Absorbed by <u>Sampler</u>	Total <u>Recovery</u>
Aceton	<u>u 1.0 t1</u>			
1	38.6	-	· _	er -
2	38.4	•_	-	-
3	37.6	-	-	· _
4	-	38.2	0.0	38.2
5	-	38.5	0.0	38.5
6	-	38.9	0.0	38.9
<u>Ethyla</u>	cetate 1.0 ml			•
7	1.1	-	-	-
8	1.2	-	-	· -
9	1.0	-	-	-
10	-	1.0	0.0	1.0
11	-	1.2	0.0	1.2
12	-	1.0	0.0	1.0
Dioxan	e 1.0 ml			
13	0.7	-	-	-
14	0.7	-	-	-
15	0.6	-	-	_ 1
16	-	0.5	0.0	0.5
17	-	0.8	0.0	0.8
18	— * * .	0.7	0.0	0.7
<u>Pyridir</u>	ne 0.1 ml			
19	45.7	-	-	· _
20	46.2	-	-	-
21	45.1	-	-	-
22	-	45.2	0.0	45.2
23	- .	45.3	0.0	45.3
24	-	43.4	0.0	43.4
Ethanet	hiol 0.1 ml	·		
25	50.5	-	-	· _
26	48.2	-	-	· 🕳
27	50.1	-	•	
28	-	49.2	1.5	50.7
29	-	47.5	1.7	49.2
30	-	48.5	1.5	50.0

TABLE VII

ORGANIC VAPOR INTERFERENCES

Item	Compound	MW	<u>Vapor, ml</u>	<u> </u>	Peak Ht.	Mercury	Interference
1	Pyridine	79.1	0.1	8.60	45.7	6.85	1.47
2	Ethanethiol	62.1	0.1	172.18	49.6	6.35	27.1
3	Benzene	78.1	0.4	163.1	35.2	4.51	36.2
4	Toluene	92,1	0.5	66.44	13.1	1.68	39.6
5	p-Xylene	106.2	0.5	24.4	4.7	0.60	40.7
6	Acetone	58.1	1.0	687.6	38.2	4.89	140.6
7	Dioxane	88.1	1.0	189.4	0.7	0.09	2104.0
8	Ethylacetate	88.1	1.0	436.1	1.1	0.14	3115.3

TABLE VIII

NANOGRAMS MEDCURY PER SQUARE INCH

	Bla	nk	Air Sample		
	Impurity	Mercury	Impurity	Mercury	
	2.59	4.07	110.0	2.88	
	3.29	4.48	85.0	3.80	
	1.61	3.29	80.0	4.54	
	2.91	3.67	58.0	4.40	
	1.68	4.10	94.0	5.95	
	2.11	5.66	98.0	4.77	
				•	
Mean	2.37	4.21	87.5	4.39	
S.D.	0.68	0.82	17.8	1.02	
S.M.E.	0.28	0.33	. 7.3	0.42	

TABLE	IX
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Name	Formula	MW	Hg 7	<u>M.P.</u>
Mercuric oxide	HgO	216.61	92.60	500 ⁰ *
Mercurous oxide	Hg20	417.22	96.16	100 [°] *
Mercuric chloride	HgC1 ₂	271.52	73.88	277°
Methylmercuric hydroxide	CH 3HgOH	232.74	86.19	
Methylmercuric chloride	CH ₃HgCl	251.08	79.89	
Methylmercuric acetate	CH 3HgOOCCH 3	274.68	73.03	
Phenylmercuric chloride	C ₆ H ₅ HgC1	313.18	64.05	
Phenylmercuric acetate	C ₆ H ₅ HgOOCCH ₃	336.75	59.57	

*Decomposed by light

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TABLE X

ORGANOMERCURIAL SAMPLING ON SILVER

	M	MA	P	PMA		
	Direct to Cell	Desorbed <u>From Sampler</u>	Direct to Cell	Desorbed From Sampler		
	31.2	-	5.0	-		
	31.6	-	5.1	-		
	31.7	-	5.0	-		
	 .	45.8	-	54.7		
	-	45.2	-	68./		
	-	42.0	-	59.3		
	-	44.0	-	/3.2		
	-	37.2	-	68.7		
	31.7	-	4.9	-		
	31.6	-	4.7	-		
	31.1	-	5.0	-		
	-	45.8	-	70.7		
	-	41.2	—	63.6		
		49.1	-	59.8		
	-	43.3	-	63.8		
	-	40.9	. –	57.3		
	31.7	. -	5.1	. .		
	31.6	-	5.5	· · · · · · · · · · · · · · · · · · ·		
	31.4	-	5.1	· -		
	31.5	-	4.8	-		
	• • •					
Меал	31.5	43.5	5.0	64.0		
S. D.	0.21	3.32	0.21	6.19		
S.M.E.	0.07	1.05	0.07	1.96		

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MMA 0.2 ml vapor . PMA 1.0 ml vapor

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TABLE XI

CONPARISON THREE AIR SAMPLERS

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Expt. <u>No.</u>	Sampler Type	Peak <u>Height</u>	Nanograms Mercury	Ng/m ³	Ng/m ³ Corrected	Mercury ppb	Unrounded <u>Numbers</u>
1	Casella	42.1	5.4	180.0	178.7	0.022	0.0217
	Unico-1	36.0	4.6	153.3	152.2	0.019	0.0185
	Unico-2	35.8	4.6	153.3	152.2	0.019	0.0185
2	Casella	35.2	4.5	150.0	149.0	0.018	0.0181
	Unico-1	36.3	4.6	153.3	152.2	0.019	0.0185
	Unico-2	36.8	4.7	153.3	152.2	0.019	0.0185
3	Casella	37.5	4.8	160.0	158.9	0.019	0.0193
	Unico-1	36.8	4.7	156.7	155.6	0.019	0.0189
	Unico-2	36.9	4.7	156.7	155.6	0.019	0.0139
4	Casella	37.9	4.8	160.0	158.9	0.019	0.0193
	Unico-1	38.2	4.9	163.3	162.2	0.020	0.0197
	Unico-2	38.0	4.9	163.3	162.2	0.020	0.0197

Note: ppb = parts per thousand million.

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TABLE XII

MERCURY IN AIR NOV. 4, 1971

Duplicate Sampling

	Nanograms					
Room	Time	Sampling Time	Hg/m ³	Mean	Percent	Difference
228	8.05	18.41	19.94		98.76	
		19.85	20.44	20.19	101.23	2.47
228	9.00	61.83	19.94		96.37	
220	,	60.85	21.43	20.69	103.57	7.20
220	9 40	60 47	217.9		106.03	
250	9.40	60.45	193.1	205.5	93.97	12.06
220	11 00	61 64	178.2		98.61	
250	11.00	60.33	183.2	180.7	101.38	2.77
777	13 00	62 51	39.68		106.23	
233	13.00	57.92	35.01	37.35	93.73	12.60
220	15 25	35 40	261.0		103.98	
220	1.2.6.1	39.57	240.9	251.0	95.98	8.00

Mean			7.62
Standard deviation	of mean	±	4.48

TABLE XIII

MERCURY IN AIR NOV. 5, 1971

Duplicate Sampling

Room	Time	Sampling <u>Time</u>	Nanograms <u> Hg/m³ </u>	Mean	Percent	Difference
228	9.30	60.43	40.01		101.03	
		60.75	39.18	39.60	98.94	2.09
228	10.30	60.88	78.23		106.65	
220		62.10	68.46	73.35	93. 33	13.32
228	14.00	39.31	97.63		108.10	
		40.32	82.99	90.31	91.89	16.21
233	14.00	59.38	19.39		98.72	
		58.95	19.88	19.64	101.22	2.50
220	14.10	31.60	77.84		106.51	
		30.14	68.31	73.08	93.47	12.04
247	14.30	60.30	761.5		101.95	
		61.21	732.3	746.9	98.04	3.91
212	14.40	55.95	16.6		90.71	
		61.42	20.0	18.30	109.28	18.57
214	15.30	23.70	270.6		101.81	
		24.46	260.9	265.8	98.16	3.65

Mean

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Standard deviation of mean

6.72

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TABLE XIV

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MERCURY IN AIR NOV. 8, 1973

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Duplicate Sampling

		Sampling	Nanograms			
Room	Time	Time	Hg/m ³	Mean	Percent	Difference
247	9:20	26.83 26.07	603.5 593.7	598.6	100.82 99.18	1.64
228	10:10	60.12 59.44	27.1 25.1	26.1	103.83 96.17	7.66
247	10:20	15.10 15.40	522.8 544.1	533.5	97.99 101.98	3.99
228	11:00	62.54 63.23	36.86 34.99	35.93	102.59 97.38	5.21
214	11:15	20.19 22.30	305.4 335.2	320.3	95.35 104.65	9.30
228	14:10	58.40 59.71	34.51 36.98	35.75	96.53 103.44	6.91
228	15:10	54.51 53.21	39.71 41.48	40.60	97.81 102.16	4.35
214	15:05	20.14 20.51	246.1 250.0	248.1	99.19 100.77	1.58
230	15:05	30.56 30.24	197.4 205.0	201.2	98.11 101.89	3.78
		JU • 44	. 20510			

Mean

Standard deviation of mean

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4.94 2.63

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<u>TANU IIV</u>

MERCURY IN OUTSIDE AIR OCT. 28, 1971

Triplicate Sampling

m í	Sampling	Nanograms Ho/m ³	Mean	Percent	Difference
Time	<u>11me</u>				
11 15	9.33	1308.7		104.51	
11.13	10.19	1211.1		96.72	
	10.08	1236.8	1252.2	98.77	7.79
11.55	9.07	1185.6		103.57	
11.00	9.27	1251.4		109.32	0.0.01
	6.34	997.1	1144.7	87.11	22.21
13.15	8.28	2558.8		107.27	
10.100	9.57	2323.2		97.39	11 02
	9.92	2274.3	2385.4	95.34	11.93
	2 00	3247 1		105.94	
13.50	5.90	2991.4		97.60	
	4.65	2956.9	3065.1	96.47	9.47
14 05	5,00	2777.4		84.60	
14.05	4.96	3420.5		104.19	
	4.70	3651.5	3283.1	111.22	26.62
14 25	4.08	2862.6		112.95	
14.23	4.85	2435.2		96.09	
	5.18	2305.3	2534.4	90.96	21.99
14 50	4.38	1033.6		116.72	
14.30	5.71	804.4		90.84	
	5.53	818.7	885.56	92.45	25.88
15 00	4.20	3333.2		118.25	
19.00	5.02	2684.0	•	95.22	
	5.12	2439.0	2818.7	86.53	23.03
15 11	4.18	1383.7		126.55	
* 7 • * *	4,99	1022.1		93. 48	
	4.81	874.5	1093.4	79.98	46.57

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7. Marky Constants

MERCURE IN CUISIDE AIR OCTOBER 28, 1971

Triplicate Sampling

	Sampling	Nanograms		. .	Difference
<u>Time</u>	Time	<u> Hg/m³ </u>	Mean	Percent	Difference
15.20	8.06	1078.2		106.01	
13.20	9.55	1123.7		110.48	
	10.23	849.3	1017.1	83.5	22.51
15.32	4.05	1300.5		112.85	
2370-	4.42	1191.0		103.35	
	5.45	965.8	1152.4	83.81	29.04
15.38	4.41	641.94		108.12	
10.30	.4.97	556.38		93.71	
	4.94	582.85	593.72	98.17	14.41
15 50	4.26	3093.0		112.80	
*7.20	5.06	2078.3		75.80	
	4.26	3054.8	2742.0	111.41	37.00
16.00	4.42	5204.5		102.14	
10.00	4.34	5300.4		104.02	
	4.88	4781.3	5095.4	93.84	10.18
16 10	4.20	3202.7		94.61	
10.10	4,26	3572.7		105.54	
	4.62	3379.8	3385.1	99.84	10.63
16.20	5.78	4866.9		96.94	
10110	4.74	5158.2		102.74	
	5.22	5036.5	5020.5	100.31	5.80
16 42	3.43	4457.2		108.37	
10.45	5.10	4014.0		97.60	
	5.09	3867.3	4112.8	94.03	14.34
16.50	5.10	8002.4		96.67	
~~	4.85	8354.7		100.92	
	4.93	8478.0	8278.4	102.41	7.74
			Mean		19.29

Mean19.29Standard Deviation of Mean11.10

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TABLE XVI

MERCURY IN AIR NOV. 15, 1971

Duplicate Sampling

Room	Time	Sampling Time Minutes	Nanograms Hg/m ³	Mean	Percent	Difference
220	8.55	20	64.27 64.43	64.35	99.83 100.12	0.29
233	9.35	60	12.66 11.87	12.27	103.18 96.74	6.44
247	11.40	20	49.20 41.44	45.32	108.56 91.44	17.12
230	13.30	31	85.21 80.39	82.80	102.91 97.09	5.82
214	14.00	22	242.70 230.70	236.70	102.53 97.47	5.06
214	16.00	20	190.00 210.40	200.20	94.91 105.09	10.18

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Mean		7.49
exceedend deviation of mean	±	5.69

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LIST OF FIGURE CAPTIONS

1. Accumulative collection of 90 nanograms mercury on silver.

2. Indoor concentrations of mercury in air, uniform and variable.

3. Sampling vapor of methylmercuric hydroxide using Geomet.

4. Response Scintrex analyzer to organomercury compounds.

5. Adsorption and desorption MMA vapor by silver.

6. Adsorption and desorption PMA vapor by silver.













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