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COLLABORATIVE STUDY OF METHOD 104 - REFERENCE METHOD FOR DETERMINATION OF BERYLLIUM EMISSION FROM STATIONARY SOURCES

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COLLABORATIVE STUDY OF METHOD 104 - REFERENCE METHOD FOR DETERMINATION OF BERYLLIUM EMISSION FROM STATIONARY SOURCES

by

Paul C. Constant, Jr., and Michael C. Sharp

Midwest Research Institute
425 Volker Boulevard
Kansas City, Missouri 64110

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EPA Project Officer: M. Rodney Midgett

Quality Assurance and Environmental Monitoring Laboratory
National Environmental Research Center
Research Triangle Park, North Carolina 27711

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FOREWORD

The collaborative study of "Method 104 Reference Method for Determination of Beryllium Emissions from Stationary Sources," was conducted under Tasks 1 and 2 of EPA Contract No. 68-02-1098, which is Midwest Research Institute Project No. 3814-C, entitled "Standardization of Stationary Sources Emission Measurement Methods." Midwest Research Institute performed an in-house evaluation of Method 104, acquired a sampling location and field facilities for the test, performed a preliminary test at this location and analyzed its results, selected four collaborators to perform sampling according to its plan of test, retrieved field data and analysis results from the collaborators, statistically analyzed the results, and prepared this two volume report.

This volume, Volume I, of the report of test, summarizes MRI's and the collaborators' activities. It presents the general plan of sampling and analysis--covering the selection of the test site, the experimental design, the selection of collaborators, the processing of samples and data, the general approach to the analysis of results and the test schedule. This is followed by discussions of site modifications, preliminary sampling and analysis by MRI, the field test, the collaborators' analyses of their samples and data, MRI's statistical analysisof the results of the test, conclusions and recommendations. Appendices contain a copy of the write-up of Method 104, and information from MRI field log.

Volume II of this report of test contains a summary of velocity profile data and velocity profiles, computer results of MRI's preliminary test, and the collaborators' results of their analysis of beryllium test samples and standard samples (prepared by NBS), and copies of the collaborators' field data sheets for the 13 runs.

The four organizations that participated as collaborators under subcontract to MRI in the test of Method 104 were the Ball Brothers Research Corporation, Boulder Colorado; the Colorado School of Mines Research Institute, Golden, Colorado; Coors Spectro-Chemical Laboratory, Golden, Colorado; and Entropy Environmentalists, Inc., Research Triangle Park; Hazen Research, Inc.; and Southern Testing and Research Labs, Inc.; performed the chemical anslysis of samples for Ball Brothers Research Corporation and Entropy Environmentalists, Inc., respectively.

The following individuals of these organizations are acknowledged for their participation in the collaborative test:

Ball Brothers Research Corporation: T. Beale, C. Dodge, S. Harmon, and Dr. George E. McVehil.

Hazen Research, Inc.: Dr. Mark A. Peters.

Colorado School of Mines Research Institute: Bob Cowan, E. F. Davis, Dr. David E. Hyatt, Carl Pearse, and R. W. Whitacre.

Coors Spectro-Chemical Laboratory: Dan Briggs, Glyndon Mondy, Fred Ranta, and Frank B. Schweitzer.

Entropy Environmentalists, Inc.: Anton S. Chaplin, Roy Doster, and Dr. James Grove.

Southern Testing and Research Labs, Inc.: Mrs. Evelyn Brady.

Special acknowledgements are made to the Coors Porcelain Company, Golden, Colorado, and Mr. D. G. Phillip of this company for providing the location for the collaborative test; to the Coors Spectro-Chemical Laboratory for providing field laboratory facilities for the collaborators and MRI; and to Dr. John B. Clements, Chief, Methods Standardization Branch, National Environmental Research Center, Environmental Protection Agency, and Rodney Midgett, Government Project Officer, Methods Standardization Branch, for their valuable suggestions in planning and design; and to the National Bureau of Standards and Dr. John Taylor of NBS for supplying standard beryllium samples.

The MRI program is being conducted under the management and technical supervision of Paul C. Constant, Jr., Head, Environmental Measurements Section of Midwest Research Institute's Physical Sciences Division, who is the program manager. Mr. William Maxwell was MRI's field supervisor at Golden, Colorado, during the 3-week collaborative test. Mr. Maxwell and Mr. George Cobb performed MRI's preliminary sampling. Mr. Thurman Oliver performed MRI's laboratory analyses of its preliminary test samples and of its standard samples. Mr. Michael Sharp was responsible for the experimental

design and statistical analyses. Miss Christine Guenther was responsible for MRI's data processing.

Approved for:

MIDWEST RESEARCH INSTITUTE

H. M. Hubbard, Director
Physical Sciences Division

4 October 1974

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SUMMARY

The Coors Porcelain Company Building No. 16, Golden, Colorado, was selected, based on eight criteria from 74 companies screened as the site for the collaborative test of "Method 104--Reference Method for Determination of Beryllium Emission from Stationary Sources," which is published in the Federal Register, 38, No. 66, Friday, 6 April 1973. The process sampled was the manufacture of different beryllium ceramic products, such as substrates and other items for the electronics and medical fields, chemical laboratories, etc. The process involves machining, grinding, blending, priming, forming and polishing. Air from the process is continuously exhausted through a series of HEPA filters before entering the 3 ft x 5 ft stack from which sampling was done simultaneously by four collaborators.

MRI performed preliminary sampling at the test location which verified the site and the experimental design for the collaborative test. This experimental design was:

$$X_{ijk} = \mu + C_i + R_j + CR_{ij} + e_{k(ij)}$$

where μ = mean,

C_i = i^{th} collaborator ($i = 1, \ldots, 4$),

R_j = j^{th} replicate ($j = 1, \ldots, 14$) and

$e_{k(ij)}$ = the measurement error associated with the k^{th} observation in the ij cell.

Since k = 1, the CR interaction term (39 degrees of freedom) can be used as the error.

This collaborative test comprised 13 runs, each on a different day, where four different collaborative organizations sampled simultaneously over the same 30-point traverse, with each point being

sampled 8 min by each collaborator. The emission levels of beryllium in the stack sampled were low, being in the neighborhood of one-tenth that of the permissible standard emission rate. In two cases, the collaborators subcontracted the chemical analysis of their samples. It is probable that one of the subcontractors had not analyzed these types of beryllium samples before by the procedures specified in Method 104. Collaborators deviated from this method with probably adverse consequences.

The four collaborators selected--Ball Brothers Research Corporation, Colorado School of Mines Research Institute, Coors Spectro-Chemical Laboratory, and Entropy Environmentalists, Inc.--collaborated in the 3-week collaborative test that took place 3-21 December 1972.

Three types of samples were prepared by the National Bureau of Standards specifically for this collaborative test: filters with BeO, ampules with suspended BeO, and ampules with soluble Be in 0.25 M HCl. These samples were given to the collaborators at Golden, Colorado.

The collaborators analyzed the test samples and standard samples at their home laboratories. The results of the collaborators were submitted to MRI who checked their calculations and found no significant errors.

There were three analyses performed. The primary one was a two-way analysis of variance to obtain the variance of repeated observations per collaborator, σ_e^2, and to obtain the variance between collaborators, σ_c^2. The analysis was done using the collaborators beryllium emission rate results. A secondary analysis was the same except beryllium-loading results were used in place of the emission rate results. The third analysis, which is also a secondary analysis, was to determine if the average velocity per sampling point per run correctly represented the geometrical variance in velocity throughout the test run even though they were measured at different times.

Pertinent results from these analyses are:

1. From the test samples:

a. The collaborator-to-collaborator variability (38% coefficient of variation) and the measurement variability (44% coefficient of variation) are approximately the same size and relatively large,

b. At a given level, measurements taken by the collaborators had a coefficient of variation of approximately 58%,

c. The daily fluctuation in beryllium emission rate at the sampling location was very large (range: 0.25 to 2.7 g/day) compared to observational errors,

d. The collaborators did not differ significantly in the amount of beryllium collected per run on their filters,

e. Almost all the differences in the collaborators' determinations of the amount of beryllium collected during a run are due to the differences in the solution (wash) portion of the samples, which included the impinger contents,

f. The measurement error for the solution determinations of beryllium is relatively larger than the measurement error in the filter determinations,

g. On the average, 77% of the beryllium collected was from the solution portion of the sample. (There were two parts to a sample, the solution portion and the filter catch.),

h. Collaborators were more repeatable and more consistent in determining beryllium from the filter, and

i. Collaborators' relative precision in the measurement of beryllium from standard samples was considerably greater than for their test samples, but the standard samples contained larger amounts of beryllium.

2. From the standard samples:

a. The components of variance, σ_e^2 and σ_c^2, are about the same size (CV $\cong$ 10%),

b. Taking into account the type of sample variance, the CV at a given level is about 25%,

c. In general, the bias is proportional to the beryllium level,

d. Usually a negative bias (about -20% on the average) was observed,

e. Generally, the bias was quite large compared to the measurement variance, and

f. The average bias on the filter samples was essentially zero, but only because large negative and positive biases canceled out.

3. From the profile analysis, it was determined that a profile plotted from the average determinations of the four collaborators correctly represented the geometrical variances in velocity throughout the run.

The major conclusions that can be drawn from this collaborative test are:

1. Using Method 104, the bias and the measurement error will be quite significant, with the bias contributing more to the unreliability of the beryllium determination. At a given level, measurements will have a coefficient of variation of approximately 58%.

2. Method 104 is adequate as written if a coefficient of variation of approximately 58% for the measurements at a given level of beryllium is acceptable.

3. The lack of precision in the results of the test samples is exclusive of the amount of beryllium collected on the filters since these measurements were repeatable by a collaborator and 77% of the error was in the beryllium measurements from the solution portion of the samples in contrast to the filter portion.

4. The biases of the solution portion of the samples are unpredictable.

5. There is not sufficient information from this test to determine whether the bias problem is due to field sampling, laboratory analysis, or both.

Based upon the conclusions that have been drawn from the results of this collaborative test, it is recommended that an investigation be undertaken to determine the reasons for the significant biases. If all collaborators had measured high or low by some significant amount, this investigation might not be needed, but because of the amount of bias and because the bias is not systematic--at times it depends on level, at other times it does not, etc.--and because it is not known whether the bias is due principally to field sampling or the analysis procedures, the investigation is needed.

I. INTRODUCTION

The Methods and Standardization Branch, National Environmental Research Center of the Environmental Protection Agency (EPA) is engaged in a program to evaluate methods, recommended and promulgated by EPA, for the measurement of pollutant emissions from stationary sources. Midwest Research Institute (MRI) is working for EPA under Contract No. 68-02-1098 to provide EPA data on the reliability and bias of the methods.

To achieve its objective, MRI plans and executes a collaborative test and evaluation for each method submitted to it by EPA. Briefly, MRI does, in the execution of a collaborative test of a method, perform an in-house evaluation of the method (which could range from a paper evaluation to a ruggedness test), provide sampling locations and facilities, select and acquire collaborators, orient the collaborators relative to the test and analysis involved, coordinate the collaborative test, retrieve field data and results of the collaborators' chemical analyses of their samples, statistically analyze results received from the collaborator, and report results to EPA.

The work activities described above were performed by MRI on its first test undertaken on the contract. The method under investigation was "Method 104--Reference Method for Determination of Beryllium Emissions from Stationary Sources," which is given on pages 8846 through 8850 of the Federal Register, 38, No. 66, Friday, 6 April 1973. (A copy of Method 104 is given in Appendix A.)

This report covers the collaborative test of Method 104 in the following order: Section II discusses the general plan for sampling and analysis--covering the selection of test site, the experimental design, the selection of collaborators, the processing of samples and data, the general approach to the analysis of test results, and the test schedule; Section III summarizes the site modifications requirements; Section IV covers preliminary sampling performed at the test site by MRI and the subsequent analysis of the field samples taken; Section V covers the collaborative field test; Section VI covers the collaborators' analysis of their field samples and standard samples prepared by the National Bureau of Standards (NBS) presenting their results; Section VII presents a discussion of the statistical analyses of test

results; Section VIII presents conclusions MRI drew from its work; and Section IX presents recommendations that are based upon the conclusions drawn. Appendices contain detailed information such as a copy of the write-up of Method 104 and MRI's field log.

II. PLAN OF SAMPLING AND ANALYSIS

The general approach used to prepare for the collaborative test of Method 104 is presented in this section. This plan comprises the selection of a test site, preparation of an experimental design, selection of collaborators, processing of field samples and data, analysis of results of the test, and the test schedule. Any deviations that were made from the planned activities are either discussed in this section or reference is made to other sections of the report.

A. Selection of Test Site

A search was made for companies involved with the mining or processing of beryllium and beryllium alloys. Seventy-four were identified as being potential test sites. These 74 companies were screened using the following criteria:

1. Continuous emissions,

2. Emissions significant enough to obtain adequate samples in a reasonable time,

3. Test locations that would require a minimum amount of modifications,

4. Companies that were desirous of their plant being a test site, and those that had cooperative personnel with whom to work,

5. Location of site such that logistics involved by potential collaborators would be reasonable, and weather conditions during test period that would not be objectionable, causing a postponement of testing or long delays,

6. Availability of test location at a site,

7. Plant operational restrictions, and

8. Available facilities for use by test crews.

After visiting the Coors Porcelain Company, Golden, Colorado, it was selected as the site for the collaborative test of Method 104. The principal reasons for its selection are:

1. The processes that feed this stack are continuous; the exhausts from these processes are fed through a series of HEPA filters before entering the stack; the stack flow rate is approximately 20,000 scfm; and the beryllium concentration is in the neighorhood of 0.6 $\mu g/m^3$.

2. The test location (see Figure 1) was a 3 ft x 5 ft rectangular stack approximately 30 ft high that is located at the northeast corner of the processing building (No. 16), a part of Coors Porcelain Company, 600 Ninth Street, Golden, Colorado. The principal modifications and equipment setups required of the test locations to ready them for collaborative testing were an 8-ft extension of the stack, with 10 2-in. ports in this extension, scaffolding on the north side of the stack (see Figure 2), a wooden platform to the south side of the stack affixed to the roof and stack, and an appropriate ladder.

3. The Coors Company was quite willing to provide a test location for the collaborative testing of beryllium; considerable testing has been done at this plant; the Spectro-Chemical Laboratory is quite knowledgable of Method 104, has the personnel and equipment to perform source emission testing, has done such testing, and this laboratory, which is approximately 1-1/2 miles from the test site, had a laboratory area for the collaborators at which they could prepare their equipment and samples.

4. The location of Coors is quite good relative to the geographic locations of potential collaborators.

5. There is no known limitation on availability of the test location. The operation is on a 24-hr basis, with the 7:00 a.m. to 3:30 p.m. shift being the principal one.

In summary, the test location shown in Figure 1, with modifications shown in Figure 2, would provide a good test site. The extension to the stack allowed for sampling to be done at approximately 1.5 diameter upstream, and 5.5 diameter downstream from any flow disturbance--a sampling configuration as shown in Figure 3. The continuous emissions of concentration 0.6 $\mu g/m^3$ would allow for an adequate sample of beryllium to be subsequently analyzed according to the procedures given in Method 104.

B. Experimental Design

The goal of the collaborative test was to obtain sufficient significant results so that the reliability and the bias of Method 104 could be determined. A major element of the collaborative test was to have an experimental design that would enable this goal to be met. Considerations that formed the bases of this design, which is given later in this section in a formal manner, are:

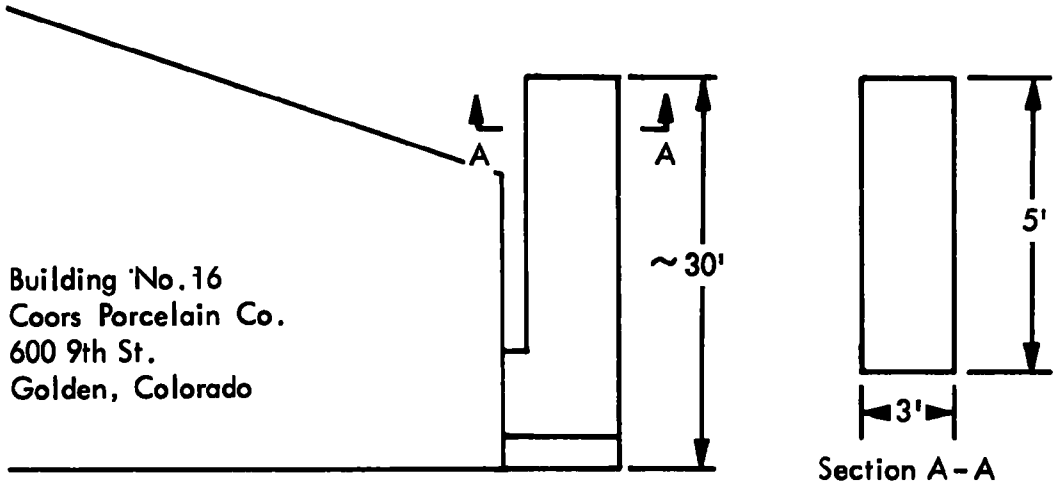


Figure 1 - Test Location

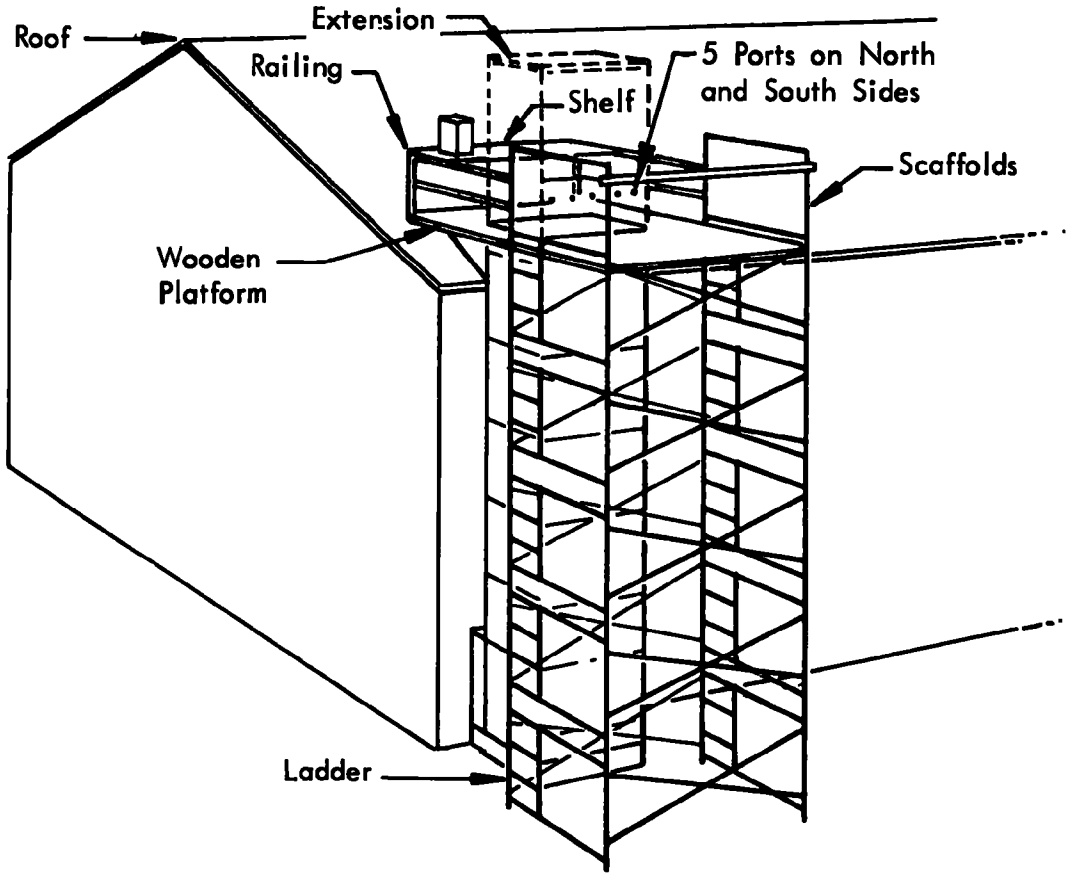


Figure 2 - Modifications for Test Location

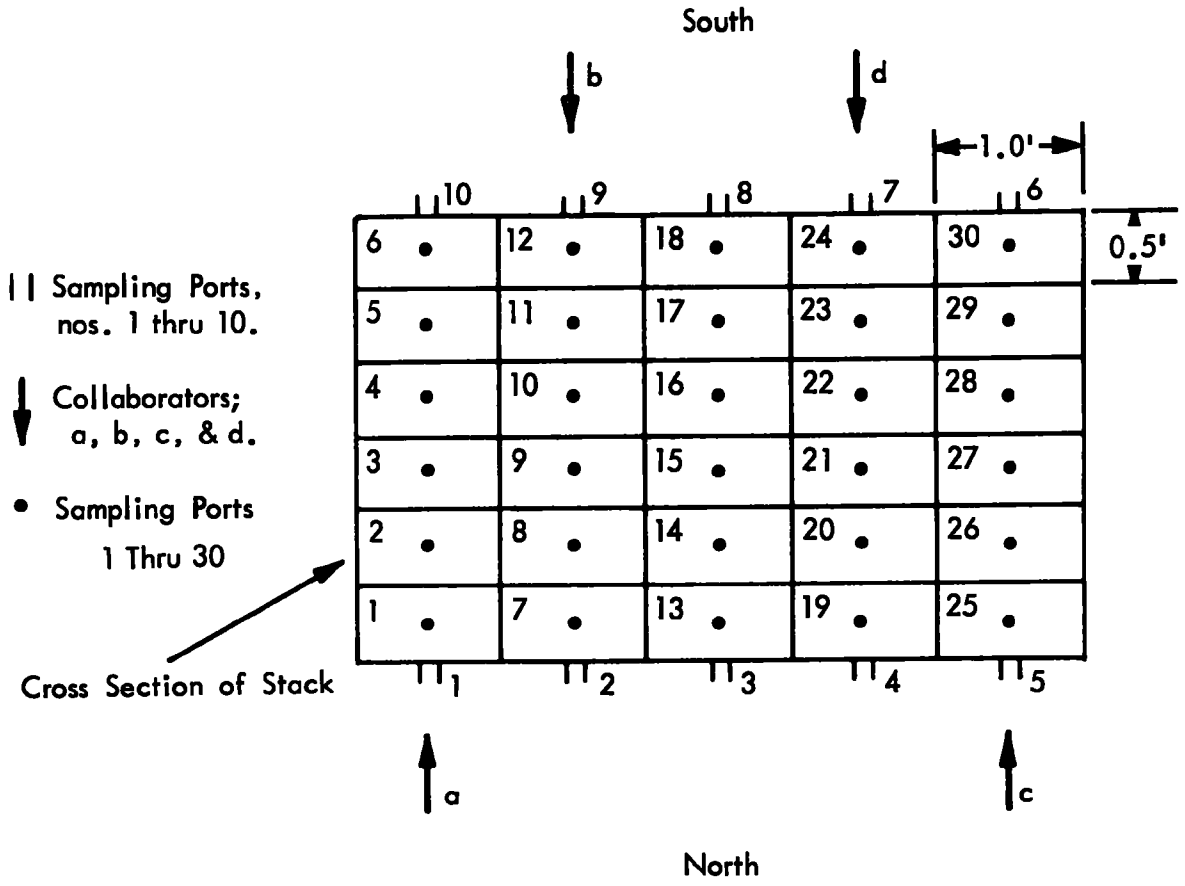


Figure 3 - Sampling Point Configuration

1. There would be a minimum of four collaborators,

2. These collaborators would sample simultaneously,

3. Sampling would be done strictly according to Method 104,

4. The beryllium content of the effluent gas stream could vary with location,

5. Concentrations of beryllium emitted from the stack could vary from day to day,

6. The duration of a run would be sufficiently long to provide an adequate sample for chemical analysis by atomic absorption techniques,

7. The level of emissions cannot be altered by spiking the gas stream or by a reduction of the production,

8. A collaborator, as per the method, could analyze each sample in parts--filter and solution catches separately--or combine the two for one determination,

9. The field test would be accomplished in 3 weeks--15 working days, and

10. Standard samples prepared by the National Bureau of Standards (NBS) would be given each collaborator for analysis.

It was desirable to execute the method in realistic fashion, i.e., to accumulate the determinations over 30 points within the stack (which are the number required because of the geometry of the stack and port locations in the stack), and to have a design so that occasional missing data would not be disastrous. On the other hand, it was also desirable to be able to account for nonuniform beryllium concentrations due to time passage and/or location within the stack. The time dependence and inhomogeneous distribution of beryllium within the stack could only be examined by incorporating these variables in an experimental design. This meant making an observation on less than 30 points.

The experimental design was:

$$X_{ijk} = \mu = C_i + L_j + CL_{ij} + e_{k(ij)},$$

where μ = mean,

C_i = i^{th} collaborator ($i = 1, \ldots, 4$),

L_j = j^{th} level ($j = 1, \ldots, 14$),

$e_{k(ij)}$ = the measurement error associated with the k^{th} observation in the ij cell,

and, since k = 1, the CR interaction (39 d.f.) can be used as the error.

The data can be considered as a factorial design with factors: collaborator (4), replicate (up to 14 at one 4-hr run per day), and "run" (solution result and filter result--although these will differ), it is nevertheless convenient to incorporate all the data into one framework.

It is necessary to include replicate as a factor because the beryllium concentration may vary from day to day.

The beryllium concentration could also vary with location, i.e., it could make a difference to the result to change ports. Therefore, each col-

laborator was ultimately assigned to approximately the same ports as every other collaborator.

C. Selection of Collaborators

A principal activity was to compile a list of potential collaborators and from this list select four to perform the testing according to Method 104. Information was obtained from EPA and from MRI's files to compile a list of over 20 potential collaborators. These organizations were screened via telephone calls to achieve a list of 18 candidate collaborators.

A Request for Proposal (RFP) was sent by MRI to these 18 candidate collaborators. This solicitation resulted in proposals being received from eight of this group. These proposals were evaluated and each was rated, considering technical capability and cost. The four selected were:

Ball Brothers Research Corporation (formerly Sierra Research Corporation),

Colorado School of Mines Research Institute,

Coors Spectro-Chemical Laboratory, and

Entropy Environmentalists, Inc.

Contract negotiations were conducted with these organizations after their selection was approved by EPA and a task order for the test was received by MRI. Hereafter, these collaborators will be referred to by randomly assigned code descriptors--collaborator 1, collaborator 2, collaborator 3, and collaborator 4.

D. Sample and Data Processing

There were five types of beryllium test samples involved that were analyzed by the collaborators. Two were field samples: the filter sample (filter with catch and loose particulate matter from the filter holder) and the acetone-wash sample (wash of probe and filter holder and impinger contents) to be taken with each 30-point run, according to Method 104. The other three types of samples were standard samples that were prepared by the National Bureau of Standards[1/] (NBS) specifically for this collaborative test:

1/ "Preparation of Reference Materials for Stationary Source Emission Analysis: Beryllium," by T. C. Rains, C. D. Olson, R. A. Velapoldi, S. A Wicks, O. Menis, and J. K. Taylor, NBSIR 74-439, March 1974.

Type 1	Type 2	Type 3
Filter, Blank		
Filter, Level 1 of BeO	Ampule X, Level 1 of Suspended BeO	Ampule Y, Level 1 of Soluble Be in 0.25 M HCl
Filter, Level 2 of BeO	Ampule X, Level 2 of Suspended BeO	Ampule Y, Level 2 of Soluble Be in 0.25 M HCl
Filter, Level 3 of BeO	Ampule X, Level 3 of Suspended BeO	Ampule Y, Level 3 of Soluble Be in 0.25 M HCl

Samples taken in the field were to be prepared after the run for transfer to the collaborator's home laboratory for analysis. This preparation was to be done according to the procedure given in Method 104.

Raw data taken by each collaborator in the field were to be recorded in duplicate by the collaborators on forms that were supplied them by MRI. One set of these forms was to be given to MRI, and the other set to be kept by the collaborator.

After the collaborators processed their field samples at their home laboratory according to procedures of and performed the calculations required by Method 104, the 37 items of information identified in Table I were to be submitted to MRI for each of the test runs.

The NBS standard samples were to be analyzed according to Method 104 and the results presented to MRI in tabular form, accordingly:

Sample Identification Number	Type Sample	Measured Be in Mg

The MRI field test coordinator was to keep a daily log which would contain sailent observations on the operations of the collaborators as well as weather data.

E. Data Analysis Approach

Each collaborator was to perform the appropriate calculations to obtain beryllium emissions results from each run (see Table I). Then raw data and the results of the chemical analyses of samples were to be provided MRI, and it was to check the calculations of the collaborators. This check was to determine if there was any gross systematic calculation errors.

TABLE I

TYPE OF RESULTS REQUIRED FROM A RUN

1. Run No.
2. Date
3. Time run began
4. Time run ended
5. Net time of test
6. Barometric pressure, in. Hg absolute
7. Standard pressure, in. Hg
8. Standard temperature, °F
9. Meter orifice pressure drop, H_2O
10. Volume dry gas at meter conditions, ft^3
11. Average gas meter temperature, °F
12. Volume dry gas at STP, ft^3
13. Total water collected, ml
14. Volume water vapor at STP, ft^3
15. Stack gas moisture, % volume
16. Assumed stack gas moisture, % volume
17. Percent CO_2
18. Percent O_2
19. Percent N_2
20. Percent excess air
21. Molecular weight of stack gas, dry
22. Molecular weight of stack gas, stack conditions
23. Stack gas specific gravity, reference to air
24. Average $\sqrt{\text{velocity, head of stack gas, } H_2O}$
25. Average stack gas temperature, °F
26. Pitot correction factor
27. Stack pressure, in. Hg absolute
28. Stack gas velocity at stack conditions, fpm
29. Stack area, ft^2
30. Stack gas flow rate at STP, scfm
31. Sampling nozzle diameter, in.
32. Percent isokinetic
33. Beryllium collected - filter, µg
34. Beryllium collected - solution, µg
35. Beryllium collected - total, µg
36. Beryllium collected - total, $\mu g/m^3$
37. Beryllium emitted per 24-hr day, g

After this preliminary check, the results of the collaborators were to be analyzed statistically. Part I of this analysis covered the field sampling results. It was a two-way analysis of variance to provide the variance of repeated sampling by each collaborator, and the variance between collaborators. Part II of the analysis covered the results of the collaborators' chemical analyses of the standard samples. The primary objectives of this analysis were to provide estimates of variance of repeated observations by a collaborator and the variance between collaborators, and to examine the biases present in the measurement of beryllium.

An important part of the statistical analysis was to determine problem areas of Method 104, and to place these generally, or if possible specifically, in one or both of the following areas: field sampling and analysis.

F. Test Schedule

There were two principal test periods--preliminary and collaborative. The preliminary test was conducted by MRI (see Section IV) to determine the readiness and suitability of the site for the collaborative test. The schedules of these tests were:

Preliminary Test by MRI

Run 1 - 6 November 1973	Run 3 - 8 November 1973
Run 2 - 7 November 1973	Run 4 - 9 November 1973

Collaborators' Test

Preparations	3 December 1973	Run 7	12 December 1973
Run 1	4 December 1973	Run 8	13 December 1973
Run 2	5 December 1973	Run 9	14 December 1973
Run 3	6 December 1973	Run 10	17 December 1973
Run 4	7 December 1973	Run 11	18 December 1973
Run 5	10 December 1973	Run 12	19 December 1973
Run 6	11 December 1973	Run 13	20 December 1973
		Run 14	21 December 1973

III. SITE PREPARATION

A line sketch of the sampling location is shown in Figure 1. The location and geometry of this stack necessitated three principal modifications to prepare it for the collaborative test: (1) extension of the stack with 2-in. diameter sampling ports in this extension; (2) scaffolding and platforms; and (3) electrical service. The Coors Spectro-Chemical Company furnished laboratory space at its building in Golden approximately 1-1/2 miles from Building 16, and electrical service at the sampling location. Figure 2 gives a sketch of the modified test site. Figure 4 provides photographs of the test site in use.

This 3 ft x 5 ft rectangular stack gives an equivalent diameter of

$$D = \frac{2\,LW}{L + W} = \frac{2 \times 3 \times 5}{3 + 5} = \frac{30}{8} = 3 \text{ ft } 9 \text{ in.}$$

By referring to Figure 101-3 of the write-up of Method 104, which is in Appendix A, it is seen that an ideal port location would be 8 diameters, or 30-ft downstream from the 90 degree bend and 2 diameters, or 7-1/2-ft upstream from the top of the stack. These dimensions would necessitate the addition of an approximately 18-ft extension to the stack, but would require a minimum of 12 sampling points. A compromise was made by using an 8-ft extension. The sampling ports were located approximately 1.5 diameters, or 6 ft from the top of the extended stack, and approximately 5.5 diameters downstream from the 90 degree bend. This location of ports, according to Figure 101-3 would require a minimum of 24 sampling points distributed over the 3 ft x 5 ft cross sectional area. To provide a better sampling scheme, 30 sampling points were selected (see Section IV) rather than the minimum of 24.

Photo 1: Looking generally east showing the 28 ft scaffold and test platform

Photo 2: Looking south showing wooden rails and sampling trains in place

Photo 3: On test platform looking south, showing shelf where all four consoles were operated

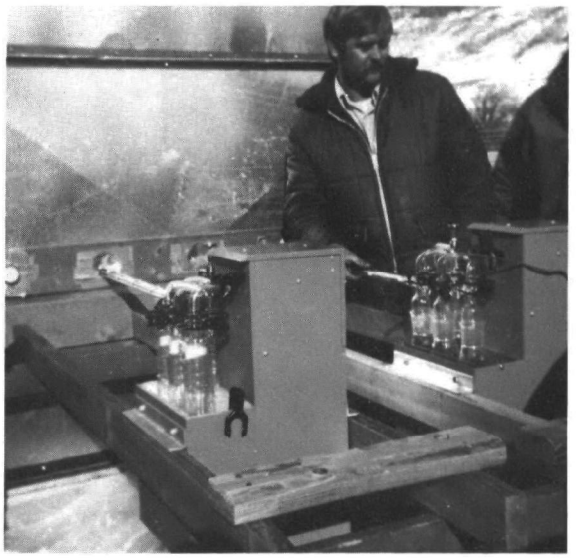


Photo 4: Looking at south ports with sampling trains in place and probes in the stack

Figure 4 - Photographs of the Test Site

IV. PRELIMINARY SAMPLING AND ANALYSIS BY MRI

After the site was prepared for sampling the first part of November 1973, MRI conducted preliminary sampling according to Method 104. The test comprised four runs (see Table II, page 22) each of which was of a different duration. Two of the runs consisted of one 6-point traverse from one port, and the remaining two runs comprised five different 6-point traverses--each traverse was made through a different port. The 6-point traverses were made to determine if sufficient beryllium (see Section II.B) would be collected, especially on a filter, during a 6-point traverse.

On Runs 1, 2, and 4, the filter catch constituted a sample and the acetone rinse of the probe and the filter holder and the impinger contents--termed solution in Table I--constituted a second sample of a run. On Run 3, there were two solution samples; the one termed front was a wash of the probe, filter holder and connecting glassware; and the other termed back was a wash of the four glass impingers and connecting glassware that followed the filter holder in the sampling train setup. (See Figure 104-1 of the write-up of Method 104 in Appendix A.)

These samples were transported to MRI by airplane where they were chemically analyzed by the procedures given in Method 104. These results of the analyses are given in Table II. These results definitely show that to provide a sufficient beryllium sample for analysis, the sampling time for a 30-point traverse sample should be 4 hr, or 8 min per point.

Gas velocity profiles for Runs 3 and 4 are shown in Figures 5 and 6. These profiles indicate that the gas flow in the stack at the sampling location is not turbulent. These profiles suggest that the beryllium concentration at any instant in time should be fairly constant throughout the sampling plane.

Based upon the results of this preliminary test, the experimental design given on pages 7-14, which only provides for 30-point sampling, was selected as the final experimental design for the collaborative test. The profiles indicated that the minimum of 24 sampling points (see Section III) could be used, but 30 points were selected to provide a better sampling scheme.

Computer results of MRI's preliminary test are given in Volume II

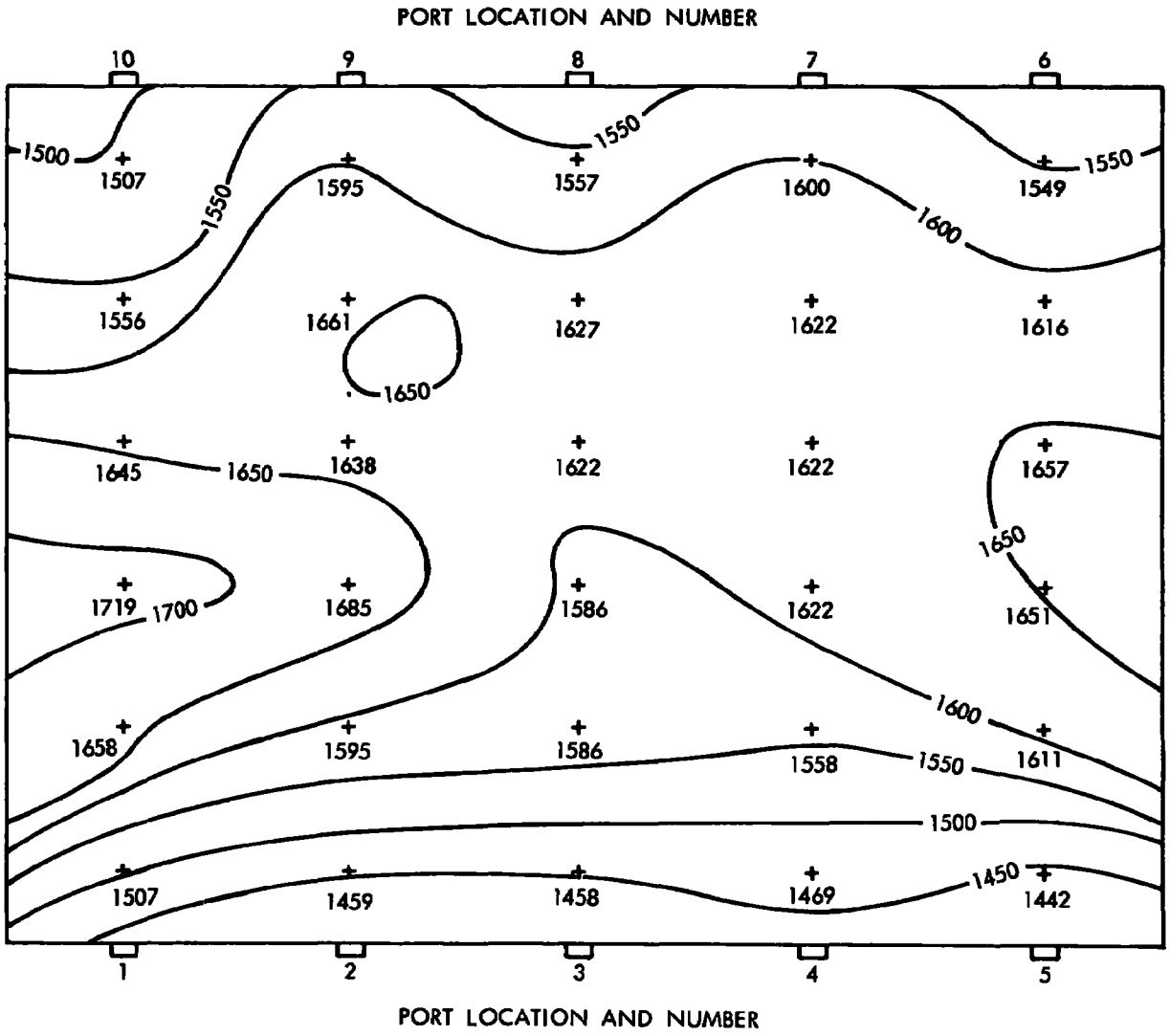


Figure 5 - Velocity Contour Profile of Run 3 of the Preliminary Test (ft/min)

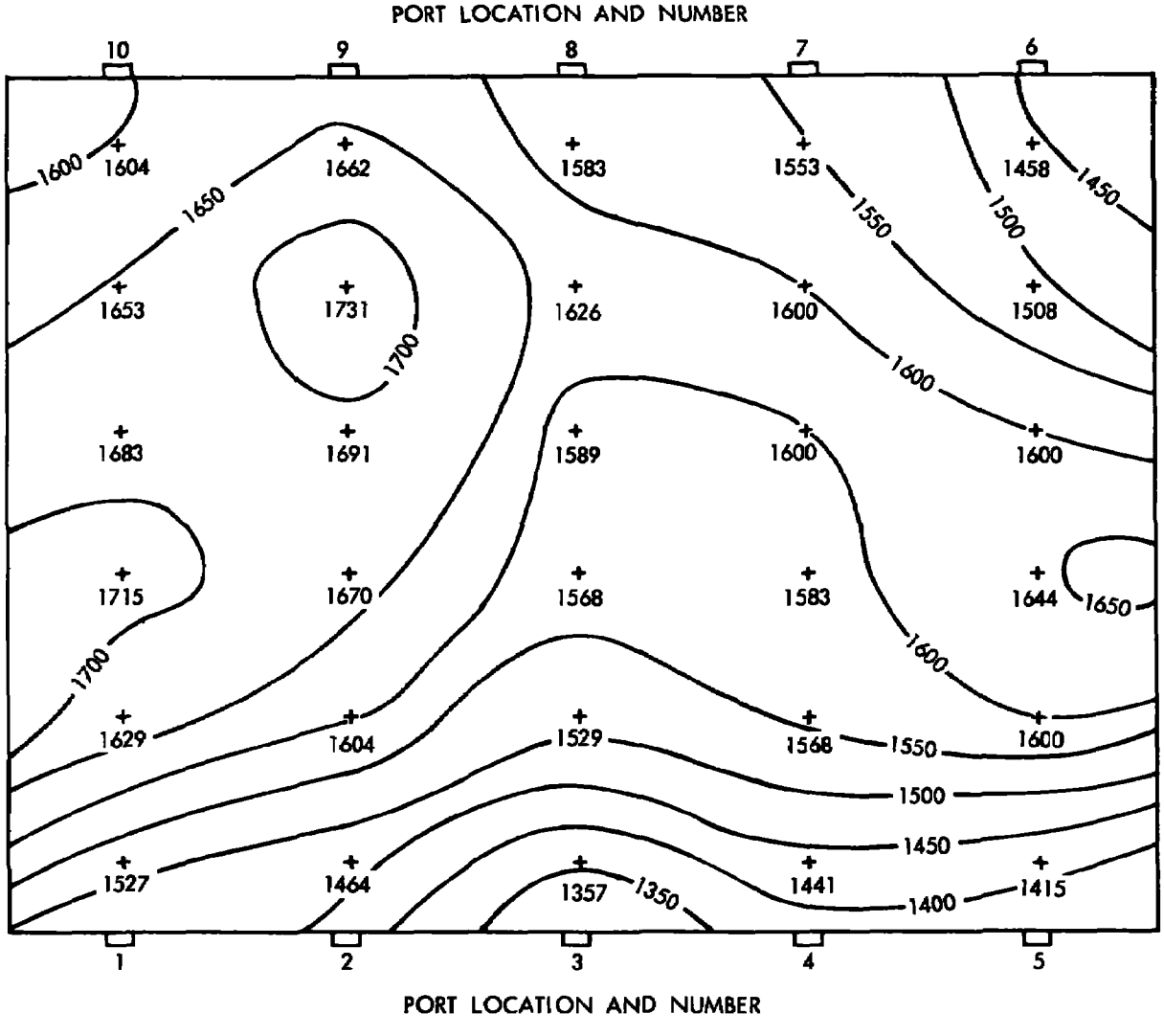


Figure 6 - Velocity Contour Profile of Run 4 of the Preliminary Test (ft/min)

TABLE II

RESULTS OF PRELIMINARY SAMPLING BY MRI

Run	Date	Sample	Time	Test Duration (min)	Traverses[a/]	Time of Sampling Per Point in Minutes	Beryllium (μg)
1	9/6	Filter	1600	24	1	4	< 0.07
		Solution					< 0.07
2	9/7	Filter	1000	48	1	8	< 0.07
		Solution					0.20
3	9/8	Filter	1400	120	5	4	< 0.07
		Solution (back)					0.14
		Solution (front)					1.38
4	9/9	Filter	0900	240	5	8	0.41
		Solution					1.29

a/ Six points per traverse. Runs 3 and 4 had five different traverses for a total of 30 sampling points per run.

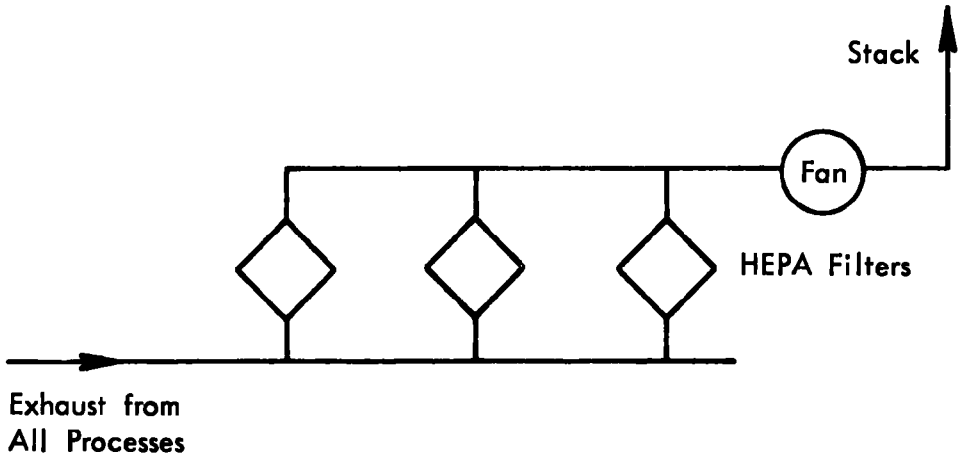
V. COLLABORATORS' FIELD SAMPLING

This section presents information on the process that was sampled, the orientation of the collaborators prior to the start of the sampling, the sampling locations, the type of sampling equipment that was used by the collaborators and generally how the test was conducted by MRI.

A. Process Sampled

At Building No. 16 of the Coors Porcelain Company (see Figure 1 page 10) where the collaborative test took place, different beryllium ceramic products are manufactured, such as substrates and other items for the electronics industry and items used in the medical field, chemical laboratories, etc. The processes involved in this manufacturing cover, such operations as machining, grinding, blending, pressing, forming, polishing, where the grinding operation, perhaps, was responsible for most of the beryllium dust or particles.

The exhaust from these processes is fed through a series of HEPA filters, as shown below, before entering the stack from which the collaborators sampled.



The manufacturing operation is continuous, on a 24-hr basis, with the 7:00 a.m. to 3:30 p.m. shift being the principal one, or the one with the greatest output. During this shift the rate of production of items is nearly constant, with the exception of personnel break periods.

B. Orientation of Collaborators

The orientation of collaborators started with MRI's solicitation for candidate collaborators and culminated with a meeting at the test site at the beginning of the first day of the test period. In each instance the principal concern was to provide the collaborators with proper information. That is, the intent was that the collaborators were to know the purpose of the test, when and where it was to take place, their responsibilities--emphasizing that Method 104 was to be followed explicitly--and to do this without biasing the collaborators in any way.

There were three modes of communication used in this orientation as summarized below.

1. Telephone: There were conversations with the collaborators (a) during the selection process in which the purpose of the test, etc., was given, and at the same time, information was obtained on their qualifications, and (b) after their selection to participate, there were discussions about type of equipment the collaborators were going to use, the test schedule, the fact that Method 104 should be strictly followed, etc.

2. Written: These included (a) the Request for Proposal MRI sent to candidate collaborators, (b) MRI's letter of acceptance to the collaborators which also included information on the test site, the test schedule, as well as general test instructions, and (c) a memorandum given to the collaborators at an on-site orientation meeting and which covered information on standard samples, their presentation of data and reporting requirement.

3. Meetings: These included (a) a site visit of the Coors Porcelain Company during the process of the selection of a test site where the purpose of the test, etc., were discussed, (b) an orientation meeting of the collaborators, which was the first activity of the test and where the test requirements, field data forms, plant regulations, the aspect of bias, etc., were discussed, and (c) interaction between the collaborators and MRI personnel during the test.

C. Sampling Location

The location selected in the planning stage of the test was used for the collaborative test, as well as MRI's preliminary testing. This location is described in Sections II.A and III, and is shown pictorially in Figures 1 and 2 on page 10, Figure 3 on page 11, and Figure 4 on page 18.

D. Sampling Equipment Used

The sampling equipment used by the four collaborators conformed to the requirements of Method 104; in each case the equipment was principally that manufactured by the Research Appliance Corporation. Notations made by MRI's field coordinator about equipment are given in Section A of Appendix B.

Figure 4 on page 18 gives some photographs of the type probes (Pyrex inserts), sampling trains and console units that were used.

MRI had sufficient sampling equipment on site to equip a collaborator and provide others with spare parts and materials if such became necessary. Most of the collaborators had spare glassware and other materials of their own.

The information reported to MRI by the four collaborators about the sampling equipment they used in the field is given below.

1. Collaborator 1: "The equipment used for collecting the samples was an RAC Train Staksamplr, Model 2343 manufactured by Research Appliance Company, Route 8, Gibsonia, Pennsylvania 15044."

2. Collaborator 2: "Beryllium sampling was accomplished by using the EPA collection train, Method 104, described in the 6 April 1973, Federal Register, It is shown schematically in Figure 7. The train consists of (1) a stainless steel nozzle connected to a 3-ft glass probe (2). Following the probe is a Millipore type A-A filter backed by a Whatman No. 41 filter, supported on a coarse fritted glass disc in a glass filter holder. Enclosing the filter assembly is a heated box (3) to maintain temperatures above the condensation point. An ice bath containing four Greenburg-Smith impingers (5) is attached to the back end of the filter by a flexible umbilical cord (4). Condensible materials are collected in the impingers. Leaving the fourth impinger, the sample stream flows through flexible tubing (6), a vacuum gage (7), needle valve (8), a leakless vacuum pump (9) in parallel with a by-pass valve (10) and a dry gas meter (11). Following this is a calibrated orifice and inclined manometer (12). A S-type pitot tube and inclined manometer (13) measures velocity pressure and stack temperature is monitored by a thermocouple connected to a potentiometer (14). Isokinetic sampling rates are maintained through the use of a nomograph which correlates the proper orifice pressure drop required for given velocity pressure and stack temperature."

3. Collaborator 3: "The equipment used was a glass EPA type sampling train manufactured by Research Appliance Company as Model 2343-5 and equipped with a Pyrex glass lined 3-ft long probe. The gas meter and

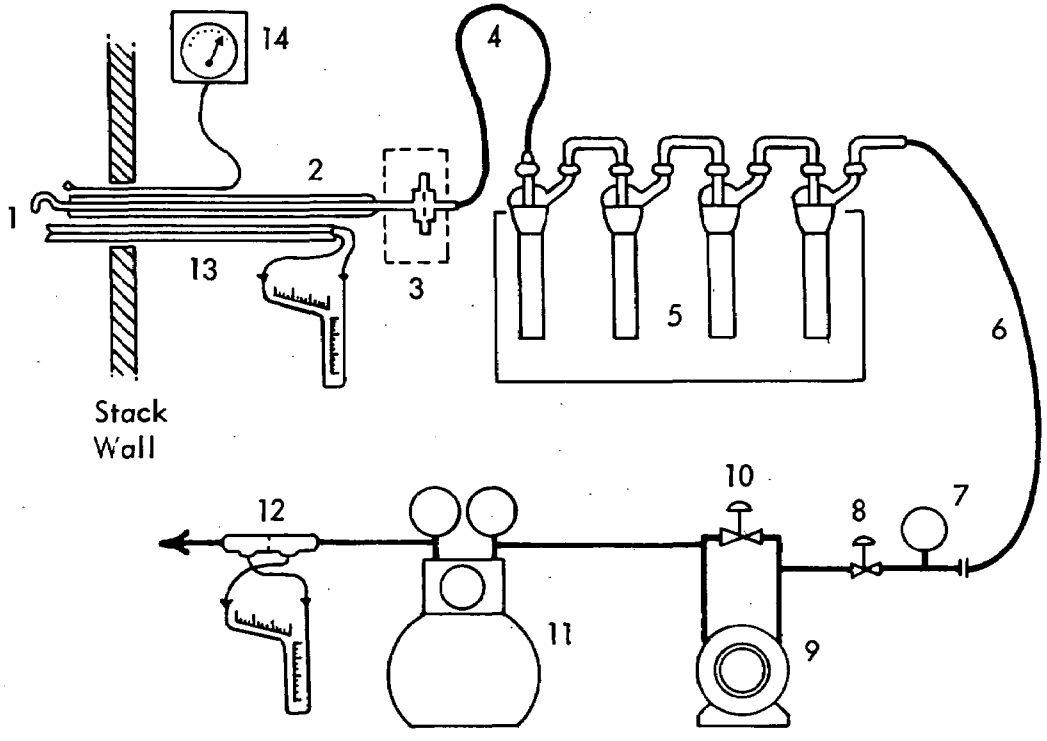


Figure 7 - Method 104 Beryllium Sampling Train

orifice meter were calibrated immediately prior to this test series. The pitot tube constant was assumed to be 0.85."

4. Collaborator 4: "Main sampling equipment was a Research Appliance Company Model "Staksamplr," with a 3 ft effective length probe (catalogue No. 2343-3). This included the meter console, sample case, umbilical cord, probe (Pyrex lined), glassware, and nomograph. A Dwyer Manufacturing Company Model 115 inclined Manometer (-0.05 to +0.25 in. H_2O) was used for velocity pressure measurements in place of the vertical inclined manometer attached to the meter console. The filter paper used was Gelman Triacetate Metricel (0.8 μm pore size, 900 mm diameter), catalogue No. GA-4 plain. The back-up filter was a Whatman No. 41. Stack temperatures were measured with a Rochester Model 1748 dial thermometer (25°-125°F). Acetone used in clean-up of probe, filter holder, and impingers was from Fisher Scientific Company, catalogue No. A-18."

E. Conduct Collaborative Test

The collaborative test of Method 104 was conducted according to its experimental design (see Section II.B) and the planned test started on 3 December 1973 and ended on 21 December. The first activity on Monday morning, 3 December was an orientation of the collaborators at the Coors Spectro-Chemical Laboratory building. After this meeting, the collaborators were shown their field laboratory area, and the test location. The collaborators spent the remainder of the day preparing for the first run that took place on Tuesday, 4 December 1973.

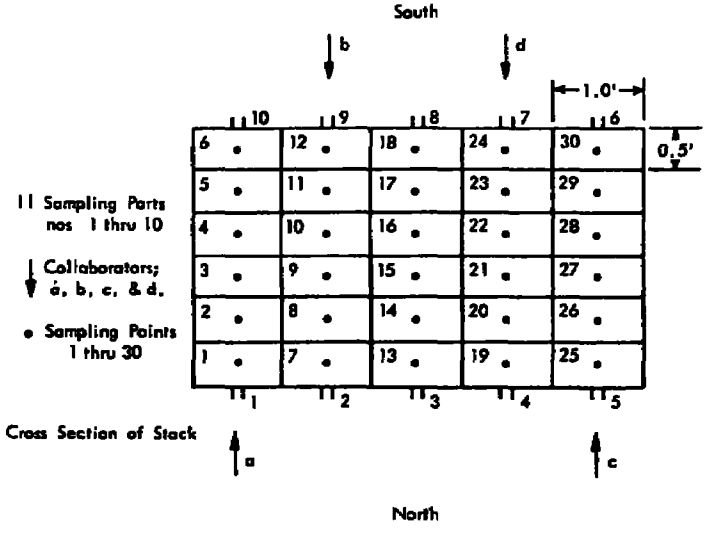
1. Overall operations: There was one run per work day (Monday through Friday), starting 4 December, with the exception of 19 December when a severe snowstorm made sampling impossible. As a result, 13 runs of the 14-run test were achieved.

Sampling started each day generally between 9:00 and 10:00 a.m. On 2 days, testing started later. In one case, the delay was due to the lack of power, and in the other it was due to extremely high winds. (More information is given this subject in Section B of Appendix B.) The four collaborators sampled simultaneously covering the 30 sampling points (8 min per point) according to the plan shown in Figure 8. During each run, each collaborator made five traverses, sampling each from a different port, as indicated in Figure 8. For example, during Run 1, traverse 1 was made by collaborator C through port 2, collaborator A through port 4, collaborator B through port 6, and collaborator D through port 8. Ports 1 and 10 provided the same traverse (sampling 6 points of the total 30 points that constituted a run), as did 2 and 9, 3 and 8, and 4 and 7, but the points were sampled in reverse order, depending on whether the probe entered a north port (1, 2, 3, 4 and 5) or a south port (6, 7, 8, 9 and 10).

Port[a]	Run 1 Traverse[b] 1	2	3	4	5	Run 2 Traverse[b] 1	2	3	4	5	Run 3 Traverse[b] 1	2	3	4	5	Run 4 Traverse[b] 1	2	3	4	5	Run 5 Traverse[b] 1	2	3	4	5	Run 6 Traverse[b] 1	2	3	4	5	Run 7 Traverse[b] 1	2	3	4	5
1		c		a			a		c			b		d			c		b			b		c			a		d			d		a	
2	c		a			a		c			b		d				c		b			b		c			a		d			d		a
3		a			c		c			a		d			b	b			c		c			b		d			a			a			d
4	a			c		c			a		d			b			b			c		c			b			d			a			a			d
5			c		a			a		c			b		d	c		b			b			c			a		d			d		a		
6	b			d		d			b		a			c			d		a			a		d			b		c			c		b		
7		b			d		d			b		a			c	d		a			a		d			b		c			c		b		
8	d		b			b		d			c		a				a			d		d			a			c			b			b		c
9		d		b			b		d			c		a		a			d		d			a			c			b		b			c	
10			d		b			b		d			c		a			d		a			a		d			b		c			c		b	

Port[a]	Run 8 Traverse[b] 1	2	3	4	5	Run 9 Traverse[b] 1	2	3	4	5	Run 10 Traverse[b] 1	2	3	4	5
1		d			c		c		d		b			d	
2	c		d			d		c				b			d
3		c		d			d		c		d		b		
4			c		d			d		c		d		b	
5	d			c		c			d				d		b
6		b			a		a			b	c			a	
7			b			a		a				a			c
8	b			a		a			b				a		c
9		a			b		b			a	a		c		
10	a			b		b			a			c			a

Port[a]	Run 11 Traverse[b] 1	2	3	4	5	Run 12 Traverse[b] 1	2	3	4	5	Run 13 Traverse[b] 1	2	3	4	5
1	a			c		d			b			a			b
2		a			c		d			b	b		a		
3	c		a			b		d				b		a	
4		c		a			b		d				b		a
5			c		a			b		d	a			b	
6	d			b		a			c			d			c
7			b		d			c		a		d	c		
8		b		d			c		a		d		e		
9	b		d			c		a				c			d
10		d			b		a			c	c			d	



a/ Ports 1 and 10, 2 and 9, 3 and 8, 4 and 7, 5 and 6 constitute the same traverse except the points along the traverse are sampled in reverse order.
b/ There were five traverses per run, with each of the four collaborators sampling with five traverses but in a different order.
c/ a, b, c, and d represent the four collaborators.

Figure 8. - Thirty-Point Sampling Plan

Sampling was performed according to Method 104, with the exceptions noted in Section V.E.2 below. At the end of a run each collaborator prepared his samples--washed probe, etc., and placed catches in appropriate containers. The nonlocal collaborators performed this work at the laboratory the Coors Spectro-Chemical Laboratory provided. The local collaborators prepared their samples at their home laboratories. Field data were recorded in duplicate by each collaborator on forms that were provided by MRI. When completed, one set was given to MRI, the other set was kept by the collaborators.

The NBS samples were shipped directly to Golden, Colorado, by NBS, where MRI packaged them individually by type for each collaborator. They were packaged well to insure that there would be no loss due to damage during their transport to the collaborators' home laboratories. Each package contained identification information, but at no time was any collaborator made aware of the amount of beryllium that was in any standard sample. In addition to the identification information, each collaborator was provided the following information that was furnished by NBS:

"Notes on Sampling: Treat each filter as an individual sample and dissolved in HNO_3, $HClO_4$ and H_2SO_4 as described in the Federal Register, 38, No. 66, 6 April 1973."

"Each ampule is prescarred. In sampling an ampule, check to see if the top or neck is free of solution. If liquid is present in the top or neck of the ampule, shake or gently tap the ampule until the top is free of solution. Then gently snap the top from the body of the ampule. Transfer sample (slurry or aqueous solution) to beaker or volumetric flask using disposable pasteur capillary pipet. Rinse ampule with mineral acid and proceed with the analysis."

Each collaborator was given 30 (three of each of the 10 kinds identified on page 14) of these standard samples during the second test day in the field. The local collaborators took their standard samples to their home laboratory the same day they got them. The other collaborators shipped their standard samples by air along with their test samples.

The conduct of the test was coordinated by MRI's field coordinator. He kept a log of field activities. This log comprises Appendix B.

Raw data taken by each collaborator in the field were recorded by them on forms that were provided by MRI. These data were recorded in duplicate, with one set given to MRI; the other set was kept by the collaborators. The collaborators' field data are given in Volume II of this report.

2. Problem areas: The problem areas that were indicated by the collaborators are given below. These writeups include deviations from the method as reported by the collaborator.

a. Collaborator 1: "On several occasions during the field testing the vacuum in the sampling train would rise and the flow rate would decrease as if there were a plug somewhere in the sampling train. This occurred for no apparent reason as it was observed that the millipore filter was not wet. This situation could only be remedied by replacing the millipore filter.

Membrane filters plug easily with only a small amount of moisture present. On one particular occasion the filter had to be changed because of condensation forming in the filter holder when the sampling train was taken from inside a building to the outdoors where the temperature was 20°F. This would be a very complicating problem in climates with high humidity.

Also, paragraph 4.5.2 of Method 104 suggests that if the stack gas is in excess of 200°F that the filter holder be moved downstream of the first impinger. For this particular collaborative test condensation was observed in the sampling train up to the fourth impinger on all occasions."

b. Collaborator 2: "The EPA Method 104 called for a heated probe, but due to the low moisture content of the stack effluent, a heated probe was not used."

c. Collaborator 3: "The prescribed technique appears to be adequate with a couple of exceptions: (1) Using the recommended 100 ml of water in the first impinger resulted in a loss of enough water from evaporation to stop the desired bubbling action. With the dry climate and length of run involved, it was found necessary to use 150 ml in the second to have continuous bubbling. (2) Due to the length of each test, the silica gel became ineffective before the end of most runs, usually resulting in a net loss of water from the train. For this reason the train water "gain" can only be used to determine stack gas moisture content for relatively short test times.

Due to the cold weather encountered, it became impossible to maintain isokinetic conditions with the 3/8-in. nozzle initially used. For this reason, Run No. 9 and subsequent runs were made with an 1/4-in. nozzle."

d. Collaborator 4: "The method required that if the glassware is idle for 2 days (whether 10 ft from the beryllium source or 1,000 miles away), it must be resoaked in hydrochloric acid. This seems very arbitrary, and was not followed by us (Friday afternoon to Monday morning is 2-1/2 days)."

3. Limitations: The two major limitations of field testing were (1) the low beryllium emissions, and (2) the adverse weather. The beryllium concentrations emitted were in the neighborhood of 0.6 $\mu g/m^3$, which provided relatively low amounts of beryllium in the field samples taken by the collaborators. The total amount of beryllium sampled during a 4-hr run generally was in the neighborhood of from 1-2 µg. These values compare with from 3-16 µg of beryllium contained in the NBS standard samples given to the collaborators for analysis.

The weather during the test was generally clear, cold, and windy. The temperature ranged from 24-63°F, and at times the winds exceeded 100 miles per hour. The terrain was covered with snow. At times the test location was icy, and visibility was poor. This weather created adverse working conditions for the field personnel as well as an adverse operational environment for the field sampling equipment. Field sampling equipment, such as the console, needed to be kept indoors when not in use, to minimize an extensive equipment warm-up period prior to a test, especially for the pump of the console. Also the temperature of the impingers at times may have created some icing effects within the impinger. Generally, however, the ambient conditions did not apparently adversely affect the sampling equipment.

VI. ANALYSES OF SAMPLES

A. Analysis Equipment Used by the Collaborators

Two of the four collaborators, Nos. 1 and 3, analyzed their beryllium samples in their laboratories with their own instrumentation. The other two collaborators, Nos. 2 and 4, subcontracted the analysis work. The instrumentation used for the analysis of the test samples and the standard samples is described below.

1. Collaborator 1: A Perkin-Elmer Model 303 atomic absorption spectrophotometer, manufactured by Perkin-Elmer Corporation, Norwalk, Connecticut.

2. Collaborator 2: A Perkin-Elmer Model 303 atomic absorption spectrophotometer was used in conjunction with a Perkin-Elmer DCR1 digital readout. The lamp used was a Perkin-Elmer hollow cathode Bé lamp.

3. Collaborator 3: A Jarrell Ash Model 812-250 atomic absorption spectrometer with a Perkin Elmer Model 403 burner and a beryllium hollow cathode lamp.

4. Collaborator 4: A Perkin-Elmer 303 atomic absorption spectrophotometer equipped with N_2O-Acetylene burner New Fisher Beryllium Hollow Cathode Tube.

B. Analysis Procedure

The procedures as presented in Method 104 were generally followed. The procedures each collaborator used, as discussed by them, are given below. Collaborators 2 and 4 had the analyses performed by other companies.

1. Collaborator 1: The laboratory analyses were done in accordance with Method 104 with the following exceptions:

Paragraphs 4.8.2.1 and 4.8.2.2 both state ". . . .cool to room temperature and add 5 ml concentrated sulfuric and 5 ml concentrated perchloric acid. Then proceed with step 4.8.2.4.

This procedure was changed in that 5 ml of 3:1:1 H_2O, HNO_3, $HClO_4$ mixture was added instead of adding 5 ml of concentrated perchloric acid. This was done at the recommendation of the head of the Analytical Department. In his opinion, the use of 5 ml of perchloric acid with 5 ml of concentrated sulfuric acid and fuming presented the hazard of appreciable quantities of dehydrated perchloric acid--a sensitive explosive. He did not consider over 1 ml of $HClO_4$ safe in these circumstances.

The sensitivity of the Perkin-Elmer 303 for beryllium is listed as 0.3 µg/ml/1% absorption by the manufacturer. The observed sensitivity of the unit for this set of analyses was 0.06 µg/ml/1% absorption. The observed noise level was 0.8% absorption."

2. Collaborator 2: "Samples and standards having the same run number were analyzed at the same time.

a. Solids (BeO suspensions, filters): Samples were digested in 250 ml covered beakers using 35 ml concentrated HNO_3, 5 ml concentrated $HClO_4$ and 5 ml concentrated H_2SO_4. All acids were added at the beginning of the digestion. Samples were heated on a hot plate at low heat until fumes of sulfuric appeared (3-4 hr). Fume for 15 min. Remove watch glass and allow samples to evaporate to dryness. Continue heating at low heat until sulfuric acid is removed from sides of beaker. Cool. Add 10.00 ml of a solution containing 2.5% w/v 8-hydroxyquinoline (oxine) in 3 N HCl. Allow to stand several minutes to dissolve Be, swirling occasionally. Transfer to plastic vial and cap to prevent evaporation until ready for reading on atomic-absorption spectrophotometer (Perkin-Elmer Model 303).

b. Liquids (acetone wash solution): Sample transferred in portions to 250 ml covered beaker and evaporated to about 50 ml using boiling chip to prevent bumping. (Boiling chips were amphoteric alundum granules from Hengar Company, Philadelphia, Pennsylvania). Proceed as in procedure for solids beginning with addition of concentrated acids. After solution in HCl-oxine, samples were filtered through Whatman No. 40 paper.

Several of our own standards and blanks were digested both with and without boiling chips. There was no detectable difference between the two methods of digestion.

c. NBS Liquid standards: The contents of the ampule was transferred to a 10 ml volumetric flask containing 0.25-g oxine. Use 2.5 ml concentrated HCl for rinsing the ampule. Diluted to mark with deionized water.

d. NBS BeO suspensions: The contents of the ampule were transferred to a 250-ml beaker using 2-3 ml concentrated HCl for rinsing the ampule. Proceed with digestion under solids.

e. Preparation of standard curve: Beryllium standard concentrations used were 0, 0.200, 0.360, 0.500, 1.00, 2.00, 3.00, 4.00, and 6.00 ppm.

Standards were prepared in 2.5% w/v 8-hydroxyquinoline-3N HCl solution by appropriate dilutions of a 1,000-ppm Be standard (Sargent-Welch No. SC 16220, 1,000-ppm Be).

3. Collaborator 3: "The total sample collected from final impinger (silica gel) to probe tip was determined by atomic absorption as specified in Method 104 on a Jarrell Ash Model 82-250 atomic absorption spectrometer with a Perkin-Elmer Model 403 burner and a Beryllium Hollow Cathode Lamp. A nitrous oxide-acetylene flame was used for excitation and the absorption was measured at 234.86 nm. The samples were prepared in accordance with Method 104 with 1% potassium as the chloride, added to each sample according to the procedure of Fleet et al., as referenced in Method 104, to overcome potential interfering elements.

The beryllium concentration of each sample was calculated as described in paragraph 6.6 of Method 104 and the total beryllium emissions was calculated as in 6.7. The results obtained for both test samples and standards are attached. The water analysis represents a combination of the impinger solutions and washings from the sampling train. The filter analysis represents the material collected on the Millipore Type AA filter.

4. Collaborator 4: All glassware was cleaned and soaked in 1:1 HCl wash as per instructions.

a. Be standards were prepared from a 10-ppm standard supplied by our customer by diluting with 25% HCl to cover the range from 0.002 ppm to 1.0 ppm.

b. A vial was selected at random (No. 616) and diluted to 25 ml to establish an approximate concentration range, and approximate volume necessary to obtain averageable readings from the NULL meter. We found 10-ml volume was minimum.

c. Vial samples were transferred to a graduated 10-ml glass stoppered ampule by means of syringe with small diameter transparent plastic tube in place of needle. Vials were rinsed with small amounts of 25% HCl employing this syringe method. The total volumes were adjusted to 10 ml.

d. The 18-vial samples were analyzed using standard Be conditions as stated in instructions, i.e., UV 234.9, slit 4, etc. Three NULL meter readings were taken and averaged for each standard and sample; a curve

drawn plotting parts per million versus absorbance of standards, the concentration of the samples read from the curve, dilution factors employed, and the final parts per million of these samples recorded.

e. The 12 filters were digested as per instructions, and analyzed similarly, the curve drawn, the parts per million of samples read, dilution factor (10) employed and results reported.

f. The 13 sample filters were processed and analyzed the same as for the 12 standard filters.

g. The water-acetone samples were evaporated to dryness on a hot plate.

Each acetone sample was added to its respective water-acetone beaker and evaporated to dryness on a steam bath. Then the nitric, sulfuric, perchloric digestion and atomic absorption analyses completed same as for the standard vial samples.

C. Problem Areas

The problems of analysis encountered that were indicated by collaborator 4 who had the analysis done by another company are.

1. Primary beryllium standard: Method 104 requires use of Be powder 98% purity. Since our company is not licensed for handling Be concentrates, we requested and received a low concentrate standard solution from the company who requested these analyses.

This was not actually a "problem," but mentioned here to those who may be sending out future study samples, so they may be cognizant of the necessity of also supplying low concentrate standard solutions.

2. Establishing detection limit for our equipment: Due to instability of machine electronics it was found that scale expansion two (2) was maximum readable expansion. Going to a higher expansion and using dampening consumed too large a quantity of sample for needle to stabilize, and time required caused excessive heating of exhaust system. Lacking greater expansion, 0.05 ppm was established as the lower detection limit. We contacted Perkin-Elmer, Norwalk, Connecticut; Perkin-Elmer, Raleigh, North Carolina; and an atomic absorption authority with North Carolina Air and Water Resources, all of whom confirmed this limit as most probable for our equipment.

Use of a recorder was tried but found NULL meter readings more satisfactory.

3. Vials too small: Had difficulty transferring liquid from vial to ampule for dilution. Could not rinse cap. Too tedious and time consuming.

Another problem area reported was that regarding the 5 ml of concentrated perchloric acid described by collaborator 1 in his analysis procedure on page 30.

D. Results of Collaborators' Analyses

There are several different sets of results to report. First, there are the results of MRI's preliminary testing which are presented in Table II, Section IV; second, there are the results of the collaborators' analyses of their test samples; and third, there are the results of the analyses of standard samples prepared by the National Bureau of Standards. The latter two sets of results are presented below in the order given.

1. Test samples: The results, as received by MRI, from the chemical analysis performed by the four collaborators of their test samples are given in Volume 2. These results were checked by MRI to determine if there were any systematic or gross errors of calculations. There were no significant differences.

Table III presents a summary of the amount of beryllium collected on both the filter and the solution samples, as well as their total; beryllium loading under both standard and stack conditions; and the beryllium emission rates. These data are presented by run for each of the four collaborators. Also included in this table is a summary of the size probe tip used by each collaborator and the volume of dry gas, the average stack-gas velocity and the percent isokinetic as determined by them. In addition, this table presents MRI's comparative results from its check of the collaborators calculated results.

TABLE III

SUMMARY OF THE RESULTS OF THE COLLABORATORS' ANALYSES

Run No.	Measurement	Collaborator 1[a]	MRI	Collaborator 2	MRI	Collaborator 3[b]	MRI	Collaborator 4	MRI
	Probe Tip Diameter (in.)	0.375	0.25	--	0.375	--	0.377	--	0.304	--
	Volume Dry Gas - Standard Condition	38.6	89.8	128.57	243.1	244.25	231.87	231.81	160.905	161.01
	Average Stack Gas Velocity (FPM)	1,701	1,701	1,739	1,683	1,271	1,717	1,707	1,665	1,661
	Percent Isokinetic	76.5	100	112.1	98	96.2	91.2	92.6	99.5	99.8
	Mass Be Collected - Filter (μg)	--	0.0	0.0	0.7	0.7	0.3	0.3	0.51	0.51
1	Mass Be Collected - Solution (μg)	--	1.3	1.3	1.8	1.8	2.0	2.0	0.66	0.66
	Mass Be Collected - Total (μg)	--	1.3	1.3	2.5	2.5	2.3	2.3	1.17	1.17
	Be Loading - Standard Condition ($\mu g/Nm^3$)	--	--	0.3563	--	0.3607	--	0.3496	0.257	0.2561
	Be Loading - Stack Condition ($\mu g/m^3$)	--	0.29	0.2865	0.317	0.2882	0.28	0.2747	--	0.2049
	Be Emission Rate (g/day)	--	0.30	0.3048	0.300	0.3024	0.29	0.288	0.209	0.2088
	Probe Tip Diameter (in.)	--	0.25	--	0.375	--	0.377	--	0.304	--
	Volume Dry Gas - Standard Condition	--	91.1	91.12	247.4	245.74	229.57	230.01	156.609	159.57
	Average Stack Gas Velocity (FPM)	--	1,754	1,794	1,742	1,762	1,679	1,672	1,636	1,644
	Percent Isokinetic	--	79.1	77.4	97.1	95.3	91.7	93.3	99.7	99.3
	Mass Be Collected - Filter (μg)	--	0.0	0.0	0.83	0.83	0.2	0.2	0.45	0.45
2	Mass Be Collected - Solution (μg)	--	0.9	0.9	5.00	5.00	2.0	2.0	0.82	0.82
	Mass Be Collected - Total (μg)	--	0.9	0.9	5.83	5.83	2.2	2.2	1.27	1.27
	Be Loading - Standard Condition ($\mu g/Nm^3$)	--	--	0.3481	--	0.8360	--	0.3370	0.281	0.2805
	Be Loading - Stack Condition ($\mu g/m^3$)	--	0.28	0.2784	0.706	0.6628	0.27	0.2664	--	0.2260
	Be Emission Rate (g/day)	--	0.30	0.3048	0.705	0.7128	0.28	0.2712	0.227	0.228
	Probe Tip Diameter (in.)	--	0.25	--	0.375	--	0.377	--	0.304	--
	Volume Dry Gas - Standard Condition	--	112.9	112.98	248.7	248.38	216.32	216.47	162.531	162.76
	Average Stack Gas Velocity (FPM)	--	1,661	1,725	1,722	1,772	1,618	1,612	1,674	1,676
	Percent Isokinetic	--	102.7	99.0	97.6	94.6	88.8	90.4	98.6	98.5
	Mass Be Collected - Filter (μg)	--	0.4	0.40	0.62	0.62	0.7	0.7	0.34	0.34
3	Mass Be Collected - Solution (μg)	--	1.2	1.20	2.00	2.00	0.2	0.2	0.40	0.40
	Mass Be Collected - Total (μg)	--	1.6	1.60	2.62	2.62	0.9	0.9	0.74	0.74
	Be Loading - Standard Condition ($\mu g/Nm^3$)	--	--	0.4991	--	0.3718	--	0.1466	0.161	0.1602
	Be Loading - Stack Condition ($\mu g/m^3$)	--	0.40	0.4024	0.318	0.2982	0.12	0.1167	--	0.1302
	Be Emission Rate (g/day)	--	0.41	0.4248	0.315	0.3240	0.12	0.1152	0.134	0.1344

TABLE III (Continued)

Run No.	Measurement	Collaborator 1[a/]	MRI	Collaborator 2	MRI	Collaborator 3[b/]	MRI	Collaborator 4	MRI
	Probe Tip Diameter (in.)	--	0.25	--	0.375	--	0.377	--	0.304	--
	Volume Dry Gas - Standard Condition	--	109.2	109.26	249.6	249.61	208.39	208.45	159.322	159.36
	Average Stack Gas Velocity (FPM)		1,608	1,642	1,751	1,796	1,674	1,570	1,671	1,675
	Percent Isokinetic	--	101.8	99.8	96.8	94.3	88.5	90.0	98.1	97.9
	Mass Be Collected - Filter (μg)	--	--	--	1.60	1.60	0.5	0.5	0.82	0.72
4	Mass Be Collected - Solution (μg)	--	--	--	5.62	5.62	6.2	6.2	2.40	2.40
	Mass Be Collected - Total (μg)	--	--	--	7.22	7.22	6.7	6.7	3.12	3.12
	Be Loading - Standard Condition ($\mu g/Nm^3$)	--	--	--	--	1.0193	--	1.1327	0.692	0.6899
	Be Loading - Stack Condition ($\mu g/m^3$)	--	--	--	0.812	0.8135	0.91	0.8953	--	0.5529
	Be Emission Rate (g/day)	--	--	--	0.876	0.8928	0.88	0.8592	0.566	0.5640
	Probe Tip Diameter (in.)	--	0.25	--	0.375	--	0.377	--	0.304	--
	Volume Dry Gas - Standard Condition	--	93.3	96.07	237.1	236.05	211.30	219.07	155.190	155.20
	Average Stack Gas Velocity (FPM)	--	1,575	1,608	1,634	1,679	1,692	1,691	1,651	1,655
	Percent Isokinetic	--	88.0	88.8	97.9	94.8	83.2	87.6	97.4	97.2
	Mass Be Collected - Filter (μg)	--	0.0	0.0	0.62	0.62	0.3	0.3	0.43	0.43
5	Mass Be Collected - Solution (μg)	--	1.2	1.2	4.50	4.50	1.6	1.6	1.10	1.10
	Mass Be Collected - Total (μg)	--	1.2	1.2	5.12	5.12	1.9	1.9	1.53	1.53
	Be Loading - Standard Condition ($\mu g/Nm^3$)	--	--	0.4402	--	0.7644	--	0.3057	0.348	0.3474
	Be Loading - Stack Condition ($\mu g/m^3$)	--	0.37	0.3611	0.635	0.6138	0.25	0.2421	--	0.2764
	Be Emission Rate (g/day)	--	0.36	0.3552	0.614	0.6312	0.26	0.2496	0.280	0.2808
	Probe Tip Diameter (in.)	--	0.25	--	0.375	--	0.377	--	0.304	--
	Volume Dry Gas - Standard Condition	--	110.5	110.62	227.2	226.19	205.71	205.63	154.910	154.88
	Average Stack Gas Velocity (FPM)	--	1,591	1,627	1,639	1,682	1,537	1,533	1,600	1,600
	Percent Isokinetic	--	103.7	101.5	95.1	91.8	88.7	90.2	97.4	97.3
	Mass Be Collected - Filter (μg)	--	0.0	0.0	0.66	0.66	0.2	0.2	0.26	0.26
6	Mass Be Collected - Solution (μg)	--	0.7	0.7	3.72	3.72	1.4	1.4	2.24	2.24
	Mass Be Collected - Total (μg)	--	0.7	0.7	4.38	4.38	1.6	1.6	2.50	2.50
	Be Loading - Standard Condition ($\mu g/Nm^3$)	--	--	0.2230	--	0.6824	--	0.2742	0.570	0.5689
	Be Loading - Stack Condition ($\mu g/m^3$)	--	0.18	0.1820	0.529	0.5416	0.22	0.2186	--	0.4663
	Be Emission Rate (g/day)	--	0.18	0.1800	0.541	0.5568	0.21	0.2064	0.457	0.4560

TABLE III (Continued)

Run No.	Measurement	Collaborator 1[a]		MRI	Collaborator 2	MRI	Collaborator 3[b]	MRI	Collaborator 4	MRI
	Probe Tip Diameter (in.)	--	0.25	--	0.375	--	0.377	--	0.304	--
	Volume Dry Gas - Standard Condition	--	107.8	107.47	228.5	227.44	201.58	223.60	142.355	142.34
	Average Stack Gas Velocity (FPM)	--	1,592	1,621	1,617	1,658	1,682	1,682	1,483	1,480
	Percent Isokinetic	--	103.9	101.8	95.1	94.1	80.9	90.7	99.4	99.6
	Mass Be Collected - Filter (μg)	--	0.0	0.0	0.84	0.84	0.8	0.8	0.43	0.43
7	Mass Be Collected - Solution (μg)	--	0.9	0.9	4.50	4.50	0.7	0.7	0.63	0.63
	Mass Be Collected - Total (μg)	--	0.9	0.9	5.34	5.34	1.5	1.5	1.06	1.06
	Be Loading - Standard Condition ($\mu g/Nm^3$)	--	--	0.2951	--	0.8275	--	0.2364	0.263	0.2625
	Be Loading - Stack Condition ($\mu g/m^3$)	--	0.23	0.2343	0.706	0.6535	0.21	0.1858	--	0.2088
	Be Emission Rate (g/day)	--	0.23	0.2328	0.647	0.6624	0.22	0.1896	0.190	0.1896
	Probe Tip Diameter (in.)	--	0.25	--	0.375	--	0.377	--	0.304	--
	Volume Dry Gas - Standard Condition	--	106.14	106.23	214.8	214.62	226.79	226.69	149.372	149.52
	Average Stack Gas Velocity (FPM)	--	1,595	1,627	1,667	1,621	1,693	1,691	1,699	1,638
	Percent Isokinetic	--	102.9	100.9	89	91.3	89.8	91.7	92.0	95.5
	Mass Be Collected - Filter (μg)	--	0.0	0.0	0.68	0.68	0.7	0.7	0.36	0.36
8	Mass Be Collected - Solution (μg)	--	1.9	1.9	8.20	8.20	2.0	2.0	3.46	3.46
	Mass Be Collected - Total (μg)	--	1.9	1.9	8.88	8.88	2.7	2.7	3.82	3.82
	Be Loading - Standard Condition ($\mu g/Nm^3$)	--	--	0.6303	--	1.4581	--	0.4197	0.903	0.9003
	Be Loading - Stack Condition ($\mu g/m^3$)	--	0.50	0.4968	1.129	1.1452	0.33	0.3289	--	0.7089
	Be Emission Rate (g/day)	--	0.49	0.4944	1.172	1.1352	0.35	0.3048	0.739	0.7104
	Probe Tip Diameter (in.)	--	0.25	--	0.375	--	0.255	--	0.304	--
	Volume Dry Gas - Standard Condition	--	105.89	105.95	231.5	231.28	119.85	119.59	152.620	152.63
	Average Stack Gas Velocity (FPM)	--	1,550	1,603	1,664	1,707	1,714	1,719	1,606	1,605
	Percent Isokinetic	--	105.6	102.1	96	93.7	103.4	103.7	98.9	98.9
	Mass Be Collected - Filter (μg)	--	0.5	0.5	0.76	0.76	0.2	0.2	0.35	0.35
9	Mass Be Collected - Solution (μg)	--	1.3	1.3	9.10	9.10	1.1	1.1	0.57	0.57
	Mass Be Collected - Total (μg)	--	1.8	1.8	9.86	9.86	1.3	1.3	0.92	0.92
	Be Loading - Standard Condition ($\mu g/Nm^3$)	--	--	0.5987	--	1.5024	--	0.3831	0.213	0.2124
	Be Loading - Stack Condition ($\mu g/m^3$)	--	0.47	0.4722	1.271	1.1771	0.30	0.3011	--	0.1683
	Be Emission Rate (g/day)	--	0.45	0.4632	1.205	1.2288	0.32	0.3168	0.166	0.1656

TABLE III (Continued)

Run No.	Measurement	Collaborator 1[a]	MRI	Collaborator 2	MRI	Collaborator 3[b]	MRI	Collaborator 4	MRI
	Probe Tip Diameter (in.)	--	0.25	--	0.375	--	0.255	--	0.304	--
	Volume Dry Gas - Standard Condition	--	106.45	106.78	217.8	225.88	116.64	115.98	149.879	149.81
	Average Stack Gas Velocity (FPM)	--	1,582	1,617	1,678	1,694	1,653	1,656	1,621	1,622
	Percent Isokinetic	--	102.8	101.0	89.0	91.0	105.4	104.8	96.3	96.2
	Mass Be Collected - Filter (μg)	--	0.0	0.0	1.20	1.20	0.2	0.2	0.36	0.36
10	Mass Be Collected - Solution (μg)	--	1.9	1.9	7.67	7.67	0.2	0.2	2.60	2.60
	Mass Be Collected - Total (μg)	--	1.9	1.9	8.87	8.87	0.4	0.4	2.96	2.96
	Be Loading - Standard Condition ($\mu g/Nm^3$)	--	--	0.6271	--	1.3838	--	0.1216	0.697	0.6963
	Be Loading - Stack Condition ($\mu g/m^3$)	--	0.50	0.4997	1.129	1.0977	0.10	0.0952	--	0.5510
	Be Emission Rate (g/day)	--	0.49	0.4944	1.168	1.1376	0.10	0.0960	0.547	0.5472
	Probe Tip Diamater (in.)	--	0.25	--	0.375	--	0.255	--	0.304	--
	Volume Dry Gas - Standard Condition	--	109.90	110.02	242.3	242.19	118.76	118.65	163.660	163.65
	Average Stack Gas Velocity (FPM)	--	1,600	1,669	1,656	1,701	1,684	1,681	1,625	1,628
	Percent Isokinetic	--	103.2	99.1	99.4	93.7	102.3	102.7	99.9	99.7
	Mass Be Collected - Filter (μg)	--	0.7	0.7	6.91	6.91	1.7	1.7	5.00	5.00
11	Mass Be Collected - Solution (μg)	--	9.6	9.6	33.70	33.70	5.0	5.0	3.25	3.25
	Mass Be Collected - Total (μg)	--	10.3	10.3	40.61	40.61	6.7	6.7	8.25	8.25
	Be Loading - Standard Condition ($\mu g/Nm^3$)	--	--	3.2991	--	5.9091	--	1.9900	1.78	1.7765
	Be Loading - Stack Condition ($\mu g/m^3$)	--	2.68	2.6746	5.012	4.8639	1.62	1.6024	--	1.4754
	Be Emission Rate (g/day)	--	2.62	2.7288	4.951	5.0592	1.66	1.6464	1.47	0.4688
	Probe Tip Diameter (in.)	--	0.25	--	0.375/0.25	--	0.255	--	0.304	--
	Volume Dry Gas - Standard Condition	--	105.40	105.17	132.6	132.63	110.22	110.06	150.908	151.01
	Average Stack Gas Velocity (FPM)	--	1,611	1,610	1,585	1,622	1,586	1,587	1,635	1,633
	Percent Isokinetic	--	99.8	99.7	99.3	121.7	102.0	102.1	94.7	94.9
	Mass Be Collected - Filter (μg)	--	0.6	0.6	0.77	0.77	5.6	5.6	0.63	0.63
12	Mass Be Collected - Solution (μg)	--	3.3	3.3	4.16	4.16	1.4	1.4	1.54	1.54
	Mass Be Collected - Total (μg)	--	3.9	3.9	4.93	4.93	7.0	7.0	2.17	2.17
	Be Loading - Standard Condition ($\mu g/Nm^3$)	--	--	1.3068	--	1.3099	--	2.2414	0.508	0.5064
	Be Loading - Stack Condition ($\mu g/m^3$)	--	1.04	1.0435	1.094	1.0725	1.80	1.7841	--	0.4068
	Be Emission Rate (g/day)	--	1.03	1.0272	1.459	1.0632	1.75	1.7328	0.408	0.4056

TABLE III (Concluded)

Run No.	Measurement	Collaborator 1[a/]		MRI	Collaborator 2	MRI	Collaborator 3[b/]	MRI	Collaborator 4	MRI
	Probe Tip Diameter (in.)	--	0.25	--	0.25	--	0.255	--	0.304	--
	Volume Dry Gas - Standard Condition	--	105.67	105.78	107.4	107.41	112.96	113.08	148.909	148.86
	Average Stack Gas Velocity (FPM)	--	1,616	1,653	1,643	1,690	1,632	1,632	1,624	1,624
	Percent Isokinetic	--	100.3	98.1	100.9	97.9	101.9	102.8	95.0	94.9
	Mass Be Collected - Filter (μg)	--	0.4	0.4	0.50	0.50	0.9	0.9	0.48	0.48
13	Mass Be Collected - Solution (μg)	--	3.7	3.7	5.06	5.06	2.7	2.7	3.11	3.11
	Mass Be Collected - Total (μg)	--	4.1	4.1	5.56	5.56	3.6	3.6	3.59	3.59
	Be Loading - Standard Condition ($\mu g/Nm^3$)	--	--	1.3660	--	1.8242	--	1.122	0.851	0.8499
	Be Loading - Stack Condition ($\mu g/m^3$)	--	1.09	1.0852	1.483	1.4434	0.90	0.8859	--	0.5898
	Be Emission Rate (g/day)	--	1.08	1.0992	1.153	1.4904	0.90	0.8832	0.673	0.6696

a/ Collaborator 1 changed probe tips at the completion of the first traverse (one port of six sampling points) of Run 1 and chose to present two sets of results from Run 1; one set for each probe tip used.

b/ Collaborator 3 changed probe tips at the first traverse of Run 12 because he was not maintaining isokinetic sampling, but chose to present his results in a combined form for Run 12.

Sampling was performed isokinetically with each collaborator generally being quite close to 100%. Collaborator 3 was generally low, but for most runs was between the 90-110% requirement. Since the error in mass collection is a function of the relationship

$$\frac{\text{100\% Isokinetic Sampled}}{2}$$

for a heterogeneous, particle-size distribution; it is believed that the emitted beryllium particles were quite small; and the stream flow was not turbulent, the deviations from 100% isokinetic are not significant.

The ratio of beryllium loading (stack conditions) to beryllium emission rate for each collaborator for each run is close to unity. If the loading were based on total mass collected rather than just beryllium and the ratio were a constant, then this information could be used to show that deviations between collaborators on a run could be attributable to problems of analysis. Since the procedures of Method 104 did not require total mass information, this check cannot be made here.

2. Standard samples: A summary of the results of the National Bureau of Standards on the standard samples it prepared for this collaborative test are given in Table IV. The column of recommended values were those used by MRI in its statistical analyses.

The results of MRI's analyses of some of NBS's standard samples are given in Table V. These samples were analyzed according to Method 104, as described in the Federal Register, 38, No. 66, 6 April 1973, with the exception that $HClO_4$ was excluded from the digestion. This was done purposely to determine if there would be any significant deviation in the results from those of NBS. There were none.

The results of the collaborators' analyses of the standard samples furnished by NBS are given in Volume II. These results are combined and summarized in Table VI. Also included in this table are MRI's results of the standard samples it analyzed. The first column of the table indicates the type sample; Column 2 gives the sample identification number* range assigned by NBS; Column 3 gives NBS's measured values; Columns 4-13 give the collaborators' and MRI's values as well as the deviations of these values from the NBS values; and Columns 14 through 18 give the deviations in percentages.

* The collaborators data in Volume II are referenced to these number.

TABLE IV

NBS'S SUMMARY OF ANALYTICAL RESULTS OF ITS STANDARD BERYLLIUM SAMPLES

Sample Type	Series	Be, µg/sample		
		Atomic Absorption[a]	Fluorescence[b]	Recommended Values[c]
Filters	100-150	2.98 ± 0.06	3.27 ± 0.12	2.98 ± 0.13
	200-250	7.77 ± 0.11	8.39 ± 0.28	7.77 ± 0.24
	300-350	15.2 ± 0.17	14.8 ± 0.38	15.2 ± 0.4
Suspended Solids	400-450	3.06 ± 0.06	2.96 ± 0.04	3.06 ± 0.13
	500-550	7.38 ± 0.22	7.41 ± 0.18	7.38 ± 0.48
	600-650	15.0 ± 0.29	14.5 ± 0.37	15.0 ± 0.6
Soluble Be	700-750	3.24 ± 0.03	3.06 ± 0.12	3.24 ± 0.07
	800-850	7.87 ± 0.11	7.59 ± 0.19	7.87 ± 0.24
	900-950	15.8 ± 0.14	16.1 ± 0.4	15.8 ± 0.3

a/ Based on 10 determinations. Uncertainty is standard deviation of a single measurement.

b/ Based on six determinations. Uncertainty is standard deviation of a single measurement.

c/ Uncertainty represents 95% confidence interval.

TABLE V

RESULTS OF MRI'S ANALYSES OF BeO FILTERS, SUSPENDED BEO AND BE SOLUTIONS BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

Sample	Sample No.	Amount in µg
Filter, Filter Blank	010	0.0
Filter, Filter Blank	020	0.0
Filter, BeO	130	3.0
Filter, BeO	231	7.5
Filter, BeO	331	13.3
Ampule, Suspended BeO	414	2.7
Ampule, Suspended BeO	508	6.8
Ampule, Suspended BeO	628	14.6
Ampule, Soluble Be in 0.25 M HCl	717	3.0
Ampule, Soluble Be in 0.25 M HCl	813	7.8
Ampule, Soluble Be in 0.25 M HCl	929	14.8

TABLE VI

RESULTS OF ANALYSIS OF NBS BERYLLIUM SAMPLES BY COLLABORATORS AND MRI

	I.D. No.[a]	NBS[b] (µg)	Collaborator No. 1 Measured (µg)	Δ11[c] (µg)	Collaborator No. 2 Measured (µg)	Δ12 (µg)	Collaborator No. 3 Measured (µg)	Δ13 (µg)	Collaborator No. 4 Measured (µg)	Δ14 (µg)	MRI Measured (µg)	Δ15 (µg)	Δ11 (%)	Δ12 (%)	Δ13 (%)	Δ14 (%)	Δ15 (%)
Filter, Blank	050	--	0.0	--	0.1	0.1	0.2	0.2	0.05	0.05	0.0	--	--	--	--	--	--
Filter, Blank	to	--	0.4	0.4	0.05	0.05	0.3	0.3	0.05	0.05	--	--	--	--	--	--	--
Filter, Blank	050	--	0.0	--	0.05	0.05	0.2	0.2	0.05	0.05	--	--	--	--	--	--	--
Filter, Level 1 of BeO	100	2.98	2.7	-0.28	3.3	0.32	1.6	-1.38	3.63	0.65	3.0	0.02	-9.4	10.7	-46.3	21.8	0.6
Filter, Level 1 of BeO	to	2.98	3.5	0.52	3.21	0.23	1.6	-1.38	3.64	0.66	--	--	17.4	7.7	-46.3	22.1	--
Filter, Level 1 of BeO	150	2.98	2.8	-0.18	3.23	0.25	1.6	-1.38	3.95	0.97	--	--	-6.0	8.4	-46.3	32.6	--
Filter, Level 2 of BeO	200	7.77	7.9	0.13	8.79	1.02	5.0	-2.77	10.2	2.43	7.5	-0.27	1.7	13.1	-35.6	31.3	-3.6
Filter, Level 2 of BeO	to	7.77	8.1	0.33	8.10	0.33	4.0	-3.77	9.80	2.03	--	--	4.2	4.2	-48.5	26.1	--
Filter, Level 2 of BeO	250	7.77	8.2	0.43	6.80	-0.97	4.1	-3.67	9.75	1.98	--	--	5.5	-12.5	-47.2	25.5	--
Filter, Level 3 of BeO	300	15.2	16.0	0.8	16.7	1.50	9.0	-6.2	20.1	4.9	13.3	-1.9	5.3	9.8	-40.8	32.2	-14.3
Filter, Level 3 of BeO	to	15.2	15.0	-0.2	15.8	0.60	9.0	-6.2	21.0	5.8	--	--	-1.3	3.9	-40.8	38.2	--
Filter, Level 3 of BeO	350	15.2	15.0	-0.2	15.1	-0.10	9.0	-6.2	19.2	4.00	--	--	-1.3	-0.66	-40.8	26.3	--
Ampule X, Level 1 of Suspended BeO	400	3.06	3.0	-0.06	3.1	0.04	2.9	-0.16	0.42	-2.64	2.7	-0.36	-2.0	1.3	-5.2	-86.3	-13.3
Ampule X, Level 1 of Suspended BeO	to	3.06	3.0	-0.06	2.73	-0.33	1.5	-1.56	0.52	-2.54	--	--	-2.0	-10.8	-50.9	-83.0	--
Ampule X, Level 1 of Suspended BeO	450	3.06	2.0	-1.06	2.86	-0.2	1.4	-1.66	0.59	-2.47	--	--	-34.6	-6.5	-54.2	-80.7	--
Ampule X, Level 2 of Suspended BeO	500	7.38	7.0	-0.38	7.08	-0.30	3.3	-4.08	1.19	-6.19	6.8	-0.58	-5.1	-4.1	-55.3	-83.9	-8.5
Ampule X, Level 2 of Suspended BeO	to	7.38	7.0	-0.38	6.19	-1.19	3.5	-3.88	0.93	-6.45	--	--	-5.1	-16.1	-52.6	-87.4	--
Ampule X, Level 2 of Suspended BeO	550	7.38	7.0	-0.38	6.44	-0.94	4.6	-2.78	1.12	-6.26	--	--	-5.1	-12.7	-37.7	-84.8	--
Ampule X, Level 3 of Suspended BeO	600	15.0	14.0	-1.00	15.7	0.70	8.5	-6.50	2.60	-12.4	14.6	-0.4	-6.7	4.7	-43.3	-82.7	-2.7
Ampule X, Level 3 of Suspended BeO	to	15.0	14.0	-1.00	14.0	-1.00	10.0	-5.0	1.86	-13.14	--	--	-6.7	-6.7	-33.3	-87.6	--
Ampule X, Level 3 of Suspended BeO	650	15.0	9.0	-6.00	14.5	-0.50	7.5	-7.50	1.74	-13.26	--	--	-40.0	-3.3	-50.0	-88.4	--
Ampule Y, Level 1 of Soluble Be[d]	700	3.24	3.0	-0.24	3.2	-0.04	2.0	-1.24	2.21	-1.03	3.0	-0.24	-7.4	-1.2	-38.3	-31.8	-8.0
Ampule Y, Level 1 of Soluble Be	to	3.24	3.0	-0.24	3.08	-0.16	1.1	-2.14	2.19	-1.05	--	--	-7.4	-4.9	-66.0	-32.4	--
Ampule Y, Level 1 of Soluble Be	750	3.24	3.0	-0.24	3.24	0.0	1.4	-1.84	2.19	-1.05	--	--	-7.4	-0.0	-56.8	-32.4	--
Ampule Y, Level 2 of Soluble Be	800	7.87	7.0	-0.87	8.06	0.19	5.2	-2.67	5.13	-2.72	7.8	-0.07	-11.1	2.4	-33.9	-34.6	-0.9
Ampule Y, Level 2 of Soluble Be	to	7.87	7.0	-0.87	7.88	0.01	3.5	-4.37	5.00	-2.87	--	--	-11.1	0.13	-55.5	-36.5	--
Ampule Y, Level 2 of Soluble Be	850	7.87	7.0	-0.87	7.64	-0.23	4.5	-3.37	5.24	-2.63	--	--	-11.1	-2.9	-42.8	-33.4	--
Ampule Y, Level 3 of Soluble Be	900	15.8	15.0	-0.8	15.1	-0.70	5.2	-10.60	10.55	-5.25	14.8	-1.0	-5.1	-4.4	-67.1	-33.2	-6.8
Ampule Y, Level 3 of Soluble Be	to	15.8	12.0	-3.8	15.8	0.0	9.0	-6.8	10.80	-5.0	--	--	-24.1	0.0	-43.0	-31.6	--
Ampule Y, Level 3 of Soluble Be	950	15.8	10.0	-5.8	16.0	-0.2	6.0	-0.8	10.73	-5.07	--	--	-36.7	-1.3	-62.0	-32.0	--

a/ I.D. = NBS identification numbers; individual sample numbers lie within the ranges given.
b/ NBS = National Bureau of Standards values.
c/ Δii = Differences between NBS values and the collaborators' values.
d/ Soluble Be in 0.25 M HCl.

Collaborators 3 and 4 show significant deviations from NBS values for all the samples they analyzed. For all type samples, with the exception of the values of collaborator 4 filters, the deviations are less than NBS values. This information along with that of the test sample results (see Table III) tend to indicate that the inaccuracies lay in the analysis of samples rather than in sampling, but this is not conclusive as there is not necessary and sufficient bases for such a conclusion.

3. Velocity profile data: MRI calculated the stack velocity at each of the 30 sampling points of a run as a part of its check of the collaborators' results. These results, which are given in Volume II, form the basis for the velocity profile analyses given in Section VII.

VII. STATISTICAL ANALYSIS OF SAMPLING RESULTS

There were three analyses performed. The primary one was a two-way analysis of variance to obtain the variance of repeated observations per collaborator, σ_e^2, and to obtain the variance between collaborators, σ_c^2. The analysis was done using the collaborators beryllium emission rate results. A secondary analysis was the same except beryllium loading results were used in place of the emission rate results. The third analysis, which is also a secondary analysis, was to determine if the average velocity per sampling point per run correctly represented the geometrical variance in velocity throughout the test run even though they were measured at different times.

A. Field Test Samples

1. Analysis of beryllium emission rate: The primary analyses of the field test sample data (see Table VII) was a (two-way) analysis of variance, and the primary object of the analysis of variance was to estimate components of variance; specifically, σ_e^2 = variance of repeated observations (per collaborator), and σ_c^2 = variance between collaborators. The response is beryllium emission rate in grams per day.

Before analyzing the data, the beryllium emission rates were recalculated using the collaborators' observed values. No errors were found (simple correlation between MRI and each collaborators' results was > 99.9% in all cases), and therefore no decisions about what to do with arithmetic errors were necessary. One data point (test 4, collaborator 1) was missing. It was replaced in the analysis via the usual procedure of minimizing the error sum of squares.

In studies of this type, it is often found that the measurement error is proportional to the magnitude of the response (or some function of the response level), rather than constant, as is required by an analysis of variance assumption. This was true of the beryllium data also. The correlation between the standard deviation at a level and the level itself was +0.95 (see Table VIII). Thus, the data were transformed by a log transformation (see Table IX), and then the analysis of variance performed. The transformation z = log (100 • beryllium emission rate (g/day) = log (100 y) was used for convenience.

TABLE VII

BERYLLIUM EMISSION RATES (g/DAY) FROM RUNS 1 THROUGH 13

Test	Collaborator C1	C2	C3	C4
1	0.30	0.30	0.29	0.209
2	0.30	0.705	0.28	0.227
3	0.41	0.315	0.12	0.134
4	0.85[a]	0.876	0.88	0.566
5	0.36	0.614	0.26	0.28
6	0.18	0.541	0.21	0.457
7	0.23	0.647	0.22	0.19
8	0.49	1.172	0.35	0.739
9	0.45	1.205	0.32	0.167
10	0.49	1.168	0.10	0.547
11	2.62	4.951	1.66	1.47
12	1.03	1.037	1.75	0.408
13	1.08	1.459	0.90	0.673

a/ Artificial: Collaborator's data missing.

TABLE VIII

STANDARD DEVIATION VERSUS LEVEL OF BERYLLIUM

Level	Average Beryllium Rate (g/day)	σ
1	0.275	0.0441
2	0.378	0.2202
3	0.245	0.1415
4	0.793	0.1664
5	0.379	0.1628
6	0.347	0.1793
7	0.322	0.2175
8	0.688	0.3607
9	0.535	0.4613
10	0.576	0.4417
11	2.675	1.5980
12	1.056	0.5485
13	1.028	0.3321

TABLE IX

BERYLLIUM DATA TRANSFORMED

Level	Collaborator C1	C2	C3	C4
1	3.40	3.40	3.37	3.04
2	3.40	4.26	3.33	3.12
3	3.71	3.45	2.48	2.59
4	4.44	4.47	4.48	4.04
5	3.58	4.12	3.26	3.33
6	2.89	3.99	3.04	3.82
7	3.14	4.17	3.09	2.94
8	3.89	4.76	3.56	4.30
9	3.81	4.79	3.47	2.81
10	3.89	4.76	2.30	4.00
11	5.57	6.20	5.11	4.99
12	4.63	4.64	5.16	3.71
13	4.68	4.98	4.50	4.21

The analysis of variance results (in terms of z) are shown in Table X.

TABLE X

ANALYSIS OF VARIANCE OF BERYLLIUM EMISSION RATE

Source	dF	SS	MS	F	EMS
Collaborator (C)	3	6.1752	2.0584	10.88[a/]	$\sigma_e^2 + 13\ \sigma_c^2$
Level (L)	12	22.0305	7.3435	38.81[a/]	$\sigma_e^2 + 4\ \sigma_L^2$
Error (E)	35	6.6220	0.1892		σ_e^2

a/ Statistically significant ($\alpha < 0.01$).

dF = Degree of freedom; SS = Sum of the squares; MS = Mean square; F = Test statistic; and EMS = Expected mean square.

Thus, we have confirmed the (obvious) result that the beryllium emission rate varied significantly from day to day, and that there were significant differences between collaborators in estimating the beryllium emission rate.

The component of variance estimates from Table X are: $\sigma_e^2 = 0.1892$, $\sigma_c^2 = 0.1438$, and $\sigma_L^2 = 1.7886$.[1/] Converting these components back to the y scale (g/day) yields the theoretical results displayed in Table XI.[2/]

TABLE XI

ERROR COMPONENTS IN BERYLLIUM EMISSION RATE (G/DAY)

Level	Average y	σe	σc	$\sqrt{\sigma_c^2 + \sigma_e^2}$
1	0.275	0.120	0.104	0.159
2	0.378	0.164	0.143	0.218
3	0.245	0.107	0.093	0.142
4	0.793	0.345	0.301	0.458
5	0.379	0.165	0.144	0.219
6	0.347	0.151	0.132	0.201
7	0.322	0.141	0.122	0.186
8	0.688	0.299	0.261	0.397
9	0.535	0.233	0.203	0.309
10	0.576	0.251	0.218	0.332
11	2.675	1.164	1.014	1.544
12	1.056	0.459	0.401	0.609
13	1.028	0.447	0.390	0.593

Thus, in theory the measurement error has a (uniform) coefficient of variation (CV) of 43.5%, and the collaborator CV is 37.9%, so that the standard deviation at a given level is theoretically 57.7% of the "true value." The average theoretical standard deviation $\sqrt{\sigma_c^2 + \sigma_e^2}$ is about 110% of the average row standard deviation as computed directly from the field results (see Table IX).

Since it is by definition impossible to run a genuine replicate during the field trial, the estimate of σ_e^2 from the analysis of variance "contains" any collaborator-level interaction that might exist. Thus, a CV of 44% within a laboratory should be regarded as an upper bound to the true value.

It is possible to estimate σ_e^2 directly by computing the variance of the differences in collaborator results at two similar levels, since in theory, the variance of the independent difference $X_1 - X_2$ is the variance of X_1 + the variance of X_2, so that the variance of $(X_1 - X_2) \cong$ two variances

1/ The variance of level averages is, of course, quite large. The value is reported for completeness.

2/ In theory, the variance components are necessarily a uniform fraction of the level itself, since a log transformation was used. (Just as theoretically the variance is independent of the level if no data transformations are made.)

(X_1) if $X_1 \cong X_2$, etc. This way of estimating σ_e^2 was employed and yielded $\sigma_e^2 = 0.1444$ (z scale), compared to $\sigma_e^2 = 0.1892$ from the analysis of variance. Of course, this estimate is also imperfect since the data do not yield exactly equal pairs of levels of Be. Nevertheless, the two estimates should bracket σ_e^2, and, since they are about the same size, it is probably true that the measurement CV is about 40%.

Summarizing:

1. The collaborator-to-collaborator variance (38% CV) and the measurement variance (44% CV) are about the same size and are sizable fractions of the true value,

2. At a given level, measurements taken by various collaborators will have a coefficient of variation of approximately 58%--this is the proper number to estimate bounds about the true value if there is no bias, and

3. The daily fluctuation in beryllium emissions rate at the sampling location was very large (range 0.25 to 2.7 g/day) compared to observational errors.

Finally, the filter only beryllium mass collected results and the solution* only beryllium mass collected results were analyzed separately. (One collaborator seldom found anything on the filter, so his results were deleted from the corresponding analysis of variance.) These analyses showed that collaborators do not differ significantly in amount of beryllium collected on the filter (except, of course, the one collaborator who did not find anything on the filter). In other words, almost all of the difference in collaborators' determinations of the amount of beryllium are due to difference in the solution determination. Also, the measurement error for the solution determination is relatively (and absolutely, of course) larger than the measurement error in the filter determination. Since, on the average 77% of the beryllium collected is from the solution, but collaborators are more repeatible and more consistent in determining beryllium from the filter, it would be better to multiply the filter results by an appropriate constant than to analyze the solution if the filter amount had a consistent ratio to the solution amount. However, this is not true (see Table XII).

* Solution is that part of the sample that results from a wash, e.g., the acetone wash of the probe and the filter holder and the impinger contents (see Section IV).

TABLE XII

RATIO OF MASS OF BERYLLIUM COLLECTED: FILTER/SOLUTION

Level	C1[a/]	C2	C3	C4
1	0	0.39	0.15	0.77
2	0	0.17	0.10	0.55
3	0.33	0.31	3.50	0.85
4	--	0.28	0.08	0.30
5	0	0.14	0.19	0.39
6	0	0.18	0.14	0.12
7	0	0.19	1.14	0.68
8	0	0.08	0.35	0.10
9	0.38	0.08	0.18	0.61
10	0	0.16	1.00	0.14
11	0.07	0.21	0.34	1.54
12	0.18	0.19	4.00	0.41
13	0.11	0.10	0.33	0.15

a/ C1's filter results were deleted from the analysis of filter only readings.

2. Analysis of beryllium loading (stack conditions): The response, beryllium loading (stack conditions), in micrograms per cubic meter was also considered, and the results compared to the analysis of variance results using beryllium emission rate (g/day) as the response. That is, the components of variance were estimated from beryllium loading data and compared to their counterparts from the analysis of beryllium emission rate. The beryllium loading data are given in Table XIII.

Because the standard deviation of a row is proportional to the response level, the data were log transformed (by $z = \log (100\ y)$, as before) before the analysis of variance was executed.

The analysis of variance results are shown in Table XIV.

The components of variance (z scale) are: $\sigma_e^2 = 0.194$, $\sigma_c^2 = 0.153$. In terms of the original scale, then, there is a theoretically uniform measurement error coefficient of variations (CV) of 44%, and a collaborator CV of 35%. These results are virtually identical with the results from the analysis of beryllium emission rate (g/day).

TABLE XIII

BERYLLIUM LOADING (STACK CONDITIONS ($\mu g/m^3$)

Level	C1	C2	C3	C4
1	0.29	0.317	0.28	0.205
2	0.28	0.706	0.27	0.226
3	0.40	0.318	0.12	0.130
4	(0.75)[a/]	0.812	0.91	0.553
5	0.37	0.635	0.25	0.276
6	0.18	0.529	0.22	0.466
7	0.23	0.706	0.21	0.209
8	0.50	1.129	0.33	0.709
9	0.47	1.271	0.30	0.168
10	0.50	0.129	0.10	0.557
11	2.68	5.012	1.62	1.475
12	1.04	1.094	1.80	0.407
13	1.09	1.483	0.90	0.590

a/ Artificial: Collaborator's data missing.

TABLE XIV

ANALYSIS OF VARIANCE FOR BERYLLIUM LOADING (STACK CONDITIONS) ($\mu g/m^3$)

Source	dF	SS	MS	F
Collaborator (C)	3	6.52781	2.176	11.22
Level (L)	12	21.8279	1.819	9.38
Error (e)	35	6.785481	0.194	--

dF = Degree of freedom.
SS = Sum of the squares.
MS = Mean square.
F = Test statistics.

In fact, the correlation between the Be loading and beryllium emission rate readings is 0.99. Therefore, the two responses, beryllium loading and beryllium emission rate, produce identical estimates of error, i.e., there is no error involved in estimating beryllium emission rate from beryllium loading data.

B. Standard Samples

The purposes of the standards data were: (1) to provide laboratory estimates of σ_e^2 and σ_c^2, to compare with the corresponding field results, and (2) to examine the biases present in the measurement of beryllium. Table XV shows the results where a response is the collaborators' determination minus the true value (NBS's value). Structurally the data are a complete three factor analysis of variance with three observations per cell. As before, the cell standard deviation is roughly proportional to the level of beryllium, so a log transformation was applied and the analysis of variance performed on the transformed data. Results are discussed in the original scale (μg of beryllium).

The analysis of variance results are shown in Table XVI. The collaborator type sample interaction is significant, and so is the three-way interaction.

It is easy to confuse the biases with the components of variances, so they will be discussed separately.

1. Bias: One collaborator (C2) exhibited essentially no bias on any of the sample types, and one more collaborator (C1) measured the filter amounts without bias. All other estimates were biased, and with one exception (C4 on filter samples) the biases are negative, i.e., the collaborators underestimate the amount of beryllium.

The CT (collaborator type) interaction term is significant because the difference in bias between collaborators is sometimes negative (C3) and sometimes positive (C4) on filter samples, but the bias (if it exists) is always negative on the other two sample types.

The CTL (collaborator, type, level) interaction term is significant because one collaborator (C1) only exhibits sizable biases at Level 3 on suspended and soluble samples, whereas the other collaborators exhibit a bias roughly proportional to the level of beryllium (if they exhibit a bias at all).

The filter samples exhibit by far the smallest average bias, but this is because the bias on filter determinations is sometimes positive and sometimes negative.

TABLE XV

STANDARD SAMPLE RESULTS, RESPONSE = READING - TRUE VALUE

(Raw Data: Collaborators' Measurements in μg)

		C1			C2			C3			C4		
Filter	Level 1	-0.28,	0.52,	-0.18	0.32,	0.23,	0.25	-1.38,	-1.38,	-1.38	0.65,	0.66,	0.97
	Level 2	0.13,	0.33,	0.43	1.02,	0.33,	-0.97	-2.77,	-3.77,	-3.67	2.43,	2.03,	1.98
	Level 3	0.8,	-0.2,	-0.2	1.5,	0.6,	-0.1	-6.2,	-6.2,	-6.2	4.9,	5.8,	4.0
Suspended	Level 1	-0.06,	-0.06,	1.06	0.04,	-0.33,	-0.2	-0.16,	-1.56,	-1.66	-2.64,	-2.54,	-2.47
	Level 2	-0.38,	-0.38,	-0.38	-0.3,	-1.19,	-0.94	-4.08,	-3.88,	-2.78	-6.19,	-6.45,	-6.26
	Level 3	-1.0,	-1.0,	-6.0	0.7,	-0.1,	-0.5	-6.5,	-5.0,	-7.5	-12.4,	-13.14,	-13.26
Soluble	Level 1	-0.24,	-0.24,	-0.24	-0.04,	-0.16,	0	-1.24,	-2.14,	-1.84	-1.03,	-1.05,	-1.05
	Level 2	-0.87,	-0.87,	-0.87	0.19,	-0.23,	0.01	-2.67,	-4.37,	-3.37	-2.72,	-2.87,	-2.6
	Level 3	-0.8,	-3.8,	-5.8	-0.7,	0,	0.2	-10.6,	-6.8,	-9.8	-5.25,	-5.0,	-5.07

NBS VALUES IN MICROGRAMS (TRUE VALUES)

	Filter	Suspended	Soluble
Level 1, True	2.98	3.06	3.24
Level 2, True	7.77	7.38	7.87
Level 3, True	15.2	15.0	15.8

AVERAGE BIAS (READING TRUE)

		C1	C2	C3	C4
Filter	Level 1	0.02	0.27	-1.38	0.76
	Level 2	0.30	0.13	-3.40	2.5
	Level 3	0.13	0.67	-6.20	4.90
Suspended	Level 1	-0.39	-0.16	-1.13	-2.55
	Level 2	-0.38	-0.81	-3.58	-6.30
	Level 3	-2.67	0.03	-6.33	-12.93
Soluble	Level 1	-0.24	-0.07	-1.74	-1.04
	Level 2	-0.87	-0.01	-3.47	-2.74
	Level 3	-3.47	-0.17	-9.07	-5.11

TABLE XVI

ANALYSIS OF VARIANCE FOR BERYLLIUM STANDARDS

Source	dF	SS	MS	F
Collaborator	3	1.5408	0.5136	30.04
Type of Sample	2	1.0466	0.5233	30.60
Level of Be	2	0.7665	0.3833	22.42
CT	6	0.3922	0.0654	3.82
CL	6	0.0030	0.0005	< 1.0
TL	4	~ 0	0	< 1.0
CTL	12	1.6596	0.1383	--
Error (e)	72	1.2312	0.0171	--

dF = Degree of freedom.
SS = Sum of the squares.
MS = Mean square.
F = Test statistic (F test).

Since one collaborator always managed to measure beryllium without bias, it is presumably not an impossible task. It would be very beneficial to distinguish this collaborators' procedures from the others, since the biases are by no means trivial in size.

2. Components of variance: Converting back to the original scale, the theoretical measurement standard error (σ_e) is 0.096 y,* i.e., in theory the coefficient of variation is 9.6%. Since replicates were performed, σ_e can be computed per level directly from the original data. The three coefficients of variation obtained this way are 11.6%, 6.3%, and 9.2%, respectively. Thus, it appears possible that 3 μg is harder to measure accurately than higher levels, i.e., the CV begins to diverge from 10% when the level of beryllium is sufficiently low. The coefficient of variation between collaborators (σ_c) is 9.7%, but the two interaction components of variance are also significant.

The "total" coefficient of variation, i.e., the coefficient of variation of readings at a given level, including all contributors, is 24.9%. The CV without the type of sample component of variance is 23.8%. Or, multiple collaborators reading a given level of beryllium in a given type sample will have a coefficient of variation 23.8%, and if (an equal mixture of) the three sample types are employed, the CV will be about 25%.

Since the measurement error CV is 10%, and since one collaborator measured without bias on all three type samples at all three levels, the difference between a CV of 25% and a CV of 10% represents error sources that could presumably be eliminated or reduced.

Since the bias situation is complicated, a table of mean square errors may be helpful in visualizing results (see Table XVII). The mean square errors are based on a sample size of one.

Summarizing:

1. The components of variance, σ_e^2 and σ_c^2, are about the same size (CV $\cong$ 10%). Taking into account the type of sample variance, the CV at a given level is about 25%.

2. In general, the bias is proportional to the amount of beryllium. One collaborator measured beryllium without any essential bias but usually a negative bias was observed (about -20%, average), and in fact, the bias is generally quite large compared to the measurement variance. Generally the bias in observing beryllium far overshadows the unreliability in the measuring process. The average bias on the filter samples was essentially zero, but only because large negative and positive biases cancelled out.

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* Where y is the true value of beryllium in micrograms (not the average bias).

TABLE XVII

MEAN SQUARE ERRORS IN THE COLLABORATORS' MEASUREMENT OF STANDARD SAMPLES

		C1	C2	C3	C4
Filter	Level 1	0.1199	0.1924	2.0239	0.6971
	Level 2	0.3296	0.2490	11.7921	4.8546
	Level 3	2.1661	2.4460	49.4371	26.0071
Suspended	Level 1	0.2781	0.1516	1.4029	6.6285
	Level 2	0.3765	0.8882	13.0485	39.9221
	Level 3	7.4260	1.9980	42.0660	169.1820
Soluble	Level 1	0.1988	0.1461	3.1688	1.2228
	Level 2	0.9890	0.2322	12.2730	7.7397
	Level 3	14.0380	2.0260	84.2620	28.1092

C. Velocity Profiles

Every velocity reading contains the influences of the time when the sampling was taken (t) and the position (P) where it was taken. The effects of t and P upon velocity must be identified before an accurate velocity profile can be drawn. Since each collaborator samples at one position at a time, only four (of 30) positions are sampled per time block.

A velocity profile could be drawn by simply averaging the velocity readings on each position and ignoring the effect of time. To check the validity of such a procedure, the t and P effects were separated for Run 1, and the results compared to the simple average estimates of the t and P effects. To accomplish this, the 120 velocity observations (in Run 1) were considered as 120 of the possible 900 (30 t's x 30 P's) treatment combinations of time and point. The analysis of variance of this incomplete design furnished estimates of the velocity at each t and P, and these estimates were compared to the simple average results. Following standard statistical terminology, the t and P effects estimated from the incomplete analysis of variance model will be called "adjusted" estimates, and the simple average results will be referred to as "unadjusted" values.

A complication arose in the analysis of variance because not all points (or times) were coupled. For instance, Points 1, 6, 7, 12, 13, 18, 19, 24, 25, and 30 (see Table XVIII) for a block uncoupled with the other points (times). In any given time block, either four of the Points 1, 6, 7,

12, 13, 18, 19, 24, 25, and 30 appear or none of these points appear, i.e., these 10 points can be interrelated but are not related to the other points. The data, then, are not really an incomplete 30 x 30 factorial but is instead a set of three (incomplete) 10 x 10 factorials.

TABLE XVIII

IDENTIFICATION OF SAMPLING POINTS[a/]

Port 10	Port 9	Port 8	Port 7	Port 6
P6	P12	P18	P24	P30
P5	P11	P17	P23	P29
P4	P10	P16	P22	P28
P3	P9	P15	P21	P27
P2	P8	P14	P20	P26
P1	P7	P13	P19	P25
Port 1	Port 2	Port 3	Port 4	Port 5

a/ See Figure 3.

Therefore, three analyses of variance were performed, and the results are shown in Table XIX.

The significantly large F-values mean that time and sampling point do have an influence on velocity. Therefore, the adjusted estimates of velocity at each point are compared to the unadjusted (average) velocities per point* (see Table XX).

There is no significant difference between the adjusted and unadjusted velocities per point. In fact, the Spearman rank correlation between the two sets of readings is +0.99. In other words, even though each particular point was observed in only four of the 30 time blocks, the average velocity reading per point is virtually the correct estimate of velocity.

* For completeness, the analysis comparison of times was also made, although it is not shown here. The results were similar.

TABLE XIX

ANALYSIS OF VARIANCE FOR VELOCITIES

A. Block A: (Points 1, 6, 7, 12, 13, 18, 19, 24, 25, 30)

Source	dF	SS	MS	F
Total	40	106,267,087		
R (μ,t)	10	106.075,422		
R (μ,P)	10	105,831,460		
R (t|μ,P)	9	398,463	44,274	25.01
R (P|μ,t)	9	154,488	17,165	9.70
Error	21	37,171	1,770	

B. Block B: (Points 2, 5, 8, 11, 14, 17, 20, 24, 26, 29)

Source	dF	SS	MS	F
Total	40	116,276,613		
R (μ,t)	10	116,050,664		
R (μ,P)	10	116,139,593		
R (t|μ,P)	9	110,370	12,263	9.44
R (P|μ,t)	9	198,044	22,005	16.94
Error	21	27,278	1,299	

C. Block C: (Points 3, 4, 9, 10, 15, 16, 21, 22, 27, 28)

Source	dF	SS	MS	F
Total	40	120,136,155		
R (μ,t)	10	119,911,193		
R (μ,P)	10	120,079,787		
R (t|μ,P)	9	18,342	2,038	1.13
R (P|μ,t)	9	186,929	20,770	11.47
Error	21	38,030	1,811	

TABLE XX

COMPARISON OF ADJUSTED VS. UNADJUSTED VELOCITIES PER SAMPLING POINT

Point	Adjusted Velocity[a/]	Rank	Unadjusted Velocity[b/]	Rank
1	1707	19	1727	20
2	1800	27	1811	27
3	1816	28	1822	28
4	1755	25	1750	22.5
5	1643	10	1644	11
6	1550	2	1549	1
7	1626	8	1614	7
8	1666	14	1661	14
9	1675	15	1657	13
10	1704	18	1700	18
11	1688	16	1689	16
12	1590	5	1607	5
13	1543	1	1563	3
14	1600	6	1608	6
15	1627	9	1626	9
16	1653	11	1642	10
17	1621	7	1618	8
18	1566	3	1561	2
19	1656	13	1646	12
20	1721	20	1716	19
21	1731	22	1727	21
22	1753	24	1753	25
23	1740	23	1750	24
24	1655	12	1672	15
25	1726	21	1744	22.5
26	1843	29	1838	29
27	1864	30	1853	30
28	1792	26	1783	26
29	1696	17	1690	17
30	1573	4	1571	4

a/ Computed from incomplete analysis of variance.
b/ Simple average reading per point.

VIII. CONCLUSIONS

This collaborative test comprised 13 runs, each on a different day, where four different collaborative organizations sampled simultaneously over the same 30-point traverse, with each point being sampled 8 min by each collaborator. The emission levels of beryllium in the stack sampled were low, being in the neighborhood of one-tenth that of the permissible standard emission rate. In two cases, the collaborators subcontracted the chemical analysis of their samples. It is probable that one of the subcontractors had not analyzed these types of beryllium samples by the procedure specified in Method 104. Collaborators deviated from this method with probable adverse consequences.

The major conclusions that can be drawn from the results of this collaborative test are:

1. Using Method 104, the bias and the measurement error will be quite significant, with the bias contributing more to the unreliability of the beryllium determination. At a given level, measurements will have a coefficient of variation of approximately 58%.

2. Method 104 is adequate as written if a coefficient of variation of approximately 58% for the field measurement results, at a given level of beryllium, is acceptable.

3. The lack of precision in the results of the test samples is exclusive of the amount of beryllium collected on the filters since these measurements were repeatble by a collaborator and 77% of the error was in the beryllium measurements from the solution samples.

4. The biases of the solution portion of the samples are unpredictable.

5. There is not sufficient information from this test to determine whether the bias problem is due to field sampling, laboratory analysis, or both.

IX. RECOMMENDATIONS

Based upon the conclusions that have been drawn from the results of this collaborative test, it is recommended that an investigation be undertaken to determine the reasons for the significant biases. If all collaborators had measured high or low by some significant amount, this investigation might not be needed, but because of the amount of bias and because the bias is not systematic--at times it depends on level, at other times it does not, etc.--and because it is not known whether or not the bias is due principally to field sampling or the analysis of samples procedures, the investigation is needed.

APPENDIX A

"METHOD 104--REFERENCE METHOD FOR DETERMINATION OF BERYLLIUM EMISSIONS FROM STATIONARY SOURCES"

measurements. The basis for such estimates shall be given in the test report.

4.4 *Preparation of sampling train.*—4.4.1 Assemble the sampling train as shown in figure 103–1. It is recommended that all glassware be precleaned by soaking in wash acid for 2 hours.

4.4.2 Leak check the sampling train at the sampling site. The leakage rate should not be in excess of 1 percent of the desired sample rate.

4.5 *Beryllium train operation.*—4.5.1 For each run, measure the velocity at the selected sampling point. Determine the isokinetic sampling rate. Record the velocity head and the required sampling rate.

4.5.2 Place the nozzle at the sampling point with the tip pointing directly into the gas stream. Immediately start the pump and adjust the flow to isokinetic conditions. At the conclusion of the test, record the sampling rate. Again measure the velocity head at the sampling point. The required isokinetic rate at the end of the period should not have deviated more than 20 percent from that originally calculated.

4.5.3 Sample at a minimum rate of 0.5 ft³/min. Samples shall be taken over such a period or periods as are necessary to determine the maximum emissions which would occur in a 24-hour period. In the case of cyclic operations, sufficient tests shall be made so as to allow determination or calculation of the emissions which would occur over the duration of the cycle. A minimum sampling time of 2 hours is recommended.

4.5.4 All pertinent data should be included in the test report.

4.6 *Sample recovery.*—4.6.1 It is recommended that all glassware be precleaned as in § 4.4.1. Sample recovery should also be performed in an area free of possible beryllium contamination. When the sampling train is moved, exercise care to prevent breakage and contamination. Set aside a portion of the acetone used in the sample recovery as a blank for analysis. The total amount of acetone used should be measured for accurate blank correction. Blanks can be eliminated if prior analysis shows negligible amounts.

4.6.2 Remove the filter and any loose particulate matter from filter holder and place in a container.

4.6.3 Clean the probe with acetone and a brush or long rod and cotton balls. Wash into the container. Wash out the filter holder with acetone and add to the same container.

4.7 *Analysis.*—4.7.1 Make the necessary preparation of samples and analyze for beryllium. Any currently acceptable method such as atomic absorption, spectrographic, fluorometric, chromatographic, or equivalent may be used.

5. *Calibration and standards*—5.1 *Sampling train.*—5.1.1 As a procedural check, sampling rate regulation should be compared with a dry gas meter, spirometer, rotameter (calibrated for prevailing atmospheric conditions), or equivalent, attached to nozzle inlet of the complete sampling train.

5.1.2 Data from this test and calculations should be shown in test report.

5.2 *Analysis.*—5.2.1 Standardization is made as suggested by the manufacturer of the instrument or the procedures for the analytical method.

6. *Calculations*—6.1 *Total beryllium emission.* Calculate the total amount of beryllium emitted from each stack per day by equation 103–2. This equation is applicable for continuous operations. For cyclic operations, use only the time per day each stack is in operation. The total beryllium emissions from a source will be the summation of results from all stacks.

$$R = \frac{W_t (v_s)_{avg} A_s}{V_{total}} \times \frac{86{,}400 \text{ seconds/day}}{10^6 \ \mu g/g}$$

where:

R = Rate of emission, g/day.
W_t = Total weight of beryllium collected, μg.
V_{total} = Total volume of gas sampled, ft³.
$(v_s)_{avg}$ = Average stack gas velocity, feet per second.
A_s = Stack area, ft².

7. *Test report.* 7.1 A test report shall be prepared which shall include as a minimum:

7.1.1 A detailed description of the sampling train used and results of the procedural check with all data and calculations made.

7.1.2 All pertinent data taken during test, the basis for any estimates made, calculations, and results.

7.1.3 A description of the test site, including a block diagram with a brief description of the process, location of the sample points in the cross section, dimensions and distances from any point of disturbance.

METHOD 104. REFERENCE METHOD FOR DETERMINATION OF BERYLLIUM EMISSIONS FROM STATIONARY SOURCES

1. *Principle and applicability*—1.1 *Principle.*—Beryllium emissions are isokinetically sampled from the source, and the collected sample is digested in an acid solution and analyzed by atomic absorption spectrophotometry.

1.2 *Applicability.*—This method is applicable for the determination of beryllium emissions in ducts or stacks at stationary sources. Unless otherwise specified, this method is not intended to apply to gas streams other than those emitted directly to the atmosphere without further processing.

2. *Apparatus*—2.1 *Sampling train.*—A schematic of the sampling train used by EPA is shown in figure 104–1. Commercial models of this train are available, although construction details are described in APTD–0581,[1] and operating and maintenance procedures are described in APTD–0576. The components essential to this sampling train are the following:

2.1.1 *Nozzle.*—Stainless steel or glass with sharp, tapered leading edge.

2.1.2 *Probe.*—Sheathed Pyrex[2] glass. A heating system capable of maintaining a minimum gas temperature in the range of the stack temperature at the probe outlet during sampling may be used to prevent condensation from occurring.

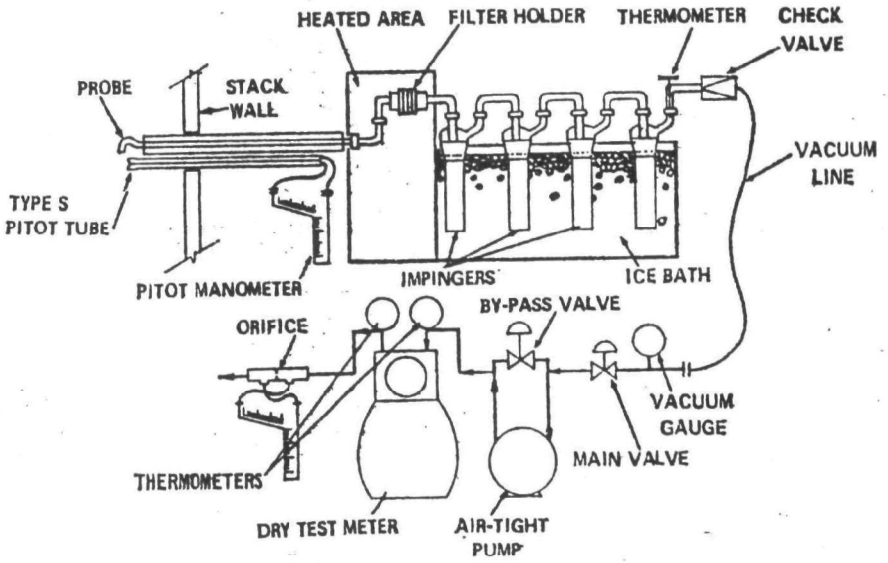

Figure 104-1. Beryllium sampling train

2.1.3 *Pitot tube.*—Type S (figure 104–2), or equivalent, with a coefficient within 5 percent over the working range, attached to probe to monitor stack gas velocity.

2.1.4 *Filter holder.*—Pyrex glass. The filter holder must provide a positive seal against leakage from outside or around the filter. A heating system capable of maintaining the filter at a minimum temperature in the range of the stack temperature may be used to prevent condensation from occurring.

2.1.5 *Impingers.*—Four Greenburg-Smith impingers connected in series with glass ball joint fittings. The first, third, and fourth impingers may be modified by replacing the tip with a ½-inch i.d. glass tube extending to one-half inch from the bottom of the flask.

2.1.6 *Metering system.*—Vacuum gauge, leakless pump, thermometers capable of measuring temperature to within 5° F, dry gas meter with 2 percent accuracy, and related equipment, described in APTD–0581, to maintain an isokinetic sampling rate and to determine sample volume.

2.1.7 *Barometer.*—To measure atmospheric pressure to ± 0.1 in Hg.

2.2 *Measurement of stack conditions (stack pressure, temperature, moisture and velocity)*—2.2.1 *Pitot tube.*—Type S, or equivalent, with a coefficient within 5 percent over the working range.

2.2.2 *Differential pressure gauge.*—Inclined manometer, or equivalent, to measure velocity head to within 10 percent of the minimum value.

[1] These documents are available for a nominal cost from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Road, Springfield, Va. 22151.

[2] Mention of trade names on specific products does not constitute endorsement by the Environmental Protection Agency.

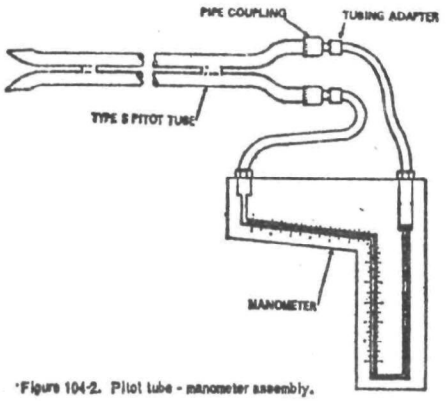

Figure 104-2. Pilot tube - manometer assembly.

2.2.3 *Temperature gage.*—Any temperature measuring device to measure stack temperature to within 5° F.

2.2.4 *Pressure gage.*—Pilot tube and inclined manometer, or equivalent, to measure stack pressure to within 0.1 in Hg.

2.2.5 *Moisture determination.*—Wet and dry bulb thermometers, drying tubes, condensers, or equivalent, to determine stack gas moisture content to within 1 percent.

2.3 *Sample recovery*—2.3.1 *Probe cleaning rod.*—At least as long as probe.

2.3.2 *Leakless glass sample bottles.*—500 ml.

2.3.3 *Graduated cylinder.*—250 ml.

2.3.4 *Plastic jar.*—Approximately 800 ml.

2.4 *Analysis*—2.4.1 *Atomic absorption spectrophotometer.*—To measure absorbance at 234.8 nm. Perkin Elmer Model 303, or equivalent, with N_2O/acetylene burner.

2.4.2 *Hot plate.*

2.4.3 *Perchloric acid fume hood.*

3. *Reagents*—3.1 *Stock reagents.*—3.1.1 *Hydrochloric acid.*—Concentrated.

3.1.2 *Perchloric acid.*—Concentrated, 70 percent.

3.1.3 *Nitric acid.*—Concentrated.

3.1.4 *Sulfuric acid.*—Concentrated.

3.1.5 *Distilled and deionized water.*

3.1.6 *Beryllium powder.*—98 percent minimum purity.

3.2 *Sampling*—3.2.1 *Filter.* — Millipore AA, or equivalent. It is suggested that a Whatman 41 filter be placed immediately against the back side of the Millipore filter as a guard against breaking the Millipore filter. In the analysis of the filter, the Whatman 41 filter should be included with the Millipore filter.

3.2.2 *Silica gel.*—Indicating type, 6 to 16 mesh, dried at 350° F for 2 hours.

3.2.3 *Distilled and deionized water.*

3.3 *Sample recovery*—3.3.1 *Distilled and deionized water.*

3.3.2 *Acetone.*—Reagent grade.

3.3.3 *Wash acid.*—1.1 V/V hydrochloric acid-water.

3.4 *Analysis.*—3.4.1 *Sulfuric acid solution, 12 N.*—Dilute 333 ml of concentrated sulfuric acid to 1 l with distilled water.

3.4.2 *25 percent V/V hydrochloric acid-water.*

3.5 *Standard beryllium solution*—3.5.1 *stock solution.*—1 μg/ml beryllium. Dissolve 10 mg of beryllium in 80 ml of 12 N sulfuric acid solution and dilute to a volume of 1000 ml with distilled water. Dilute a 10 ml aliquot to 100 ml with 25 percent V/V hydrochloric acid, giving a concentration of 1 μg/ml. This dilute stock solution should be prepared fresh daily. Equivalent strength (in beryllium) stock solutions may be prepared from beryllium salts as $BeCl_2$ and $Be(NO_3)_2$ (98 percent minimum purity).

4. *Procedure.* 4.1 Guidelines for source testing are detailed in the following sections. These guidelines are generally applicable; however, most sample sites differ to some degree and temporary alterations such as stack extensions or expansions often are required to insure the best possible sample site. Further, since beryllium is hazardous, care should be taken to minimize exposure. Finally, since the total quantity of beryllium to be collected is quite small, the test must be carefully conducted to prevent contamination or loss of sample.

4.2 Selection of a sampling site and minimum number of traverse points.

4.2.1 Select a suitable sampling site that is as close as practicable to the point of atmospheric emission. If possible, stacks smaller than 1 foot in diameter should not be sampled.

4.2.2 The sampling site should be at least 8 stack or duct diameters downstream and 2 diameters upstream from any flow disturbance such as a bend, expansion or contraction. For a rectangular cross-section, determine an equivalent diameter from the following equation:

$$D_e = \frac{2LW}{L+W} \qquad \text{eq. 104-1}$$

where:

D_e = equivalent diameter
L = length
W = width

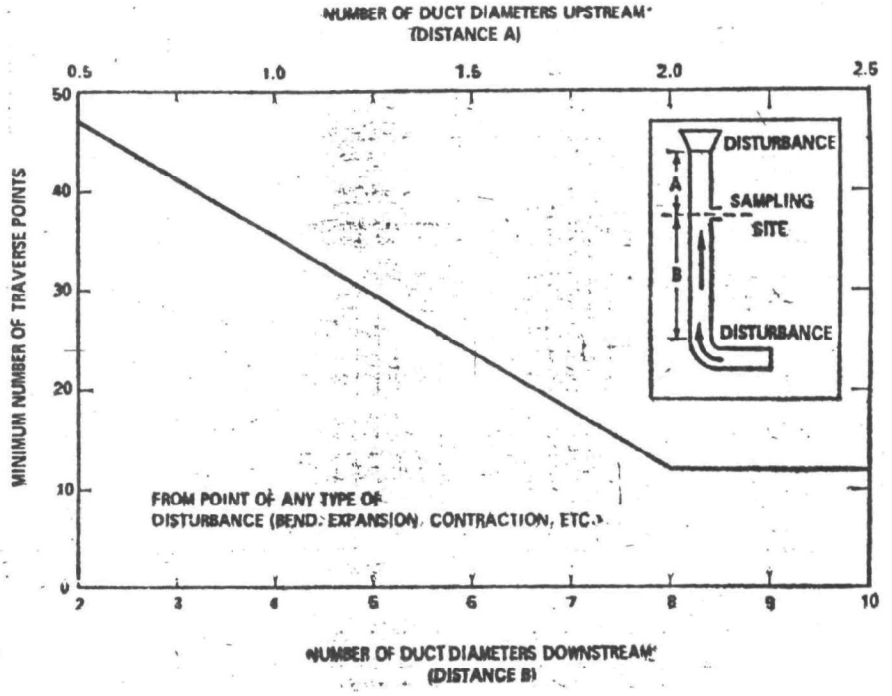

Figure 101-3. Minimum number of traverse points.

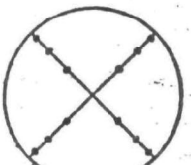

Figure 104-4. Cross section of circular stack showing location of traverse points on perpendicular diameters.

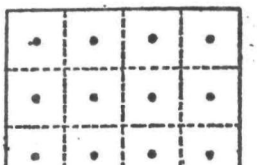

Figure 104-5. Cross section of rectangular stack divided into 12 equal areas, with traverse points at centroid of each area.

4.2.3 When the above sampling site criteria can be met, the minimum number of traverse points is four (4) for stacks 1 foot in diameter or less, eight (8) for stacks larger than 1 foot but 2 feet in diameter or less, and twelve (12) for stacks larger than 2 feet.

4.2.4 Some sampling situations may render the above sampling site criteria impractical. When this is the case, choose a convenient sampling location and use figure 104-3 to determine the minimum number of traverse points. However, use figure 104-3 only for stacks 1 foot in diameter or larger.

4.2.5 To use figure 104-3, first measure the distance from the chosen sampling location to the nearest upstream and downstream disturbances. Divide this distance by the diameter or equivalent diameter to determine the distance in terms of pipe diameters. Determine the corresponding number of traverse points for each distance from figure 104-3. Select the higher of the two numbers of traverse points, or a greater value, such that for circular stacks the number is a multiple of four, and for rectangular stacks the number follows the criteria of section 4.3.2.

4.2.6 If a selected sampling point is closer than 1 inch from the stack wall, adjust the location of that point to ensure that the sample is taken at least 1 inch away from the wall.

4.3 Cross-sectional layout and location of traverse points.

Table 104-1. Location of traverse points in circular stacks
(Percent of stack diameter from inside wall to traverse point)

Traverse point number on a diameter	Number of traverse points on a diameter											
	2	4	6	8	10	12	14	16	18	20	22	24
1	14.6	6.7	4.4	3.3	2.5	2.1	1.8	1.6	1.4	1.3	1.1	1.1
2	85.4	25.0	14.7	10.5	8.2	6.7	5.7	4.9	4.4	3.9	3.5	3.2
3		75.0	29.5	19.4	14.6	11.8	9.9	8.5	7.5	6.7	6.0	5.5
4		93.3	70.5	32.3	22.6	17.7	14.6	12.5	10.9	9.7	8.7	7.9
5			85.3	67.7	34.2	25.0	20.1	16.9	14.6	12.9	11.6	10.5
6			95.6	80.6	65.8	35.5	26.9	22.0	18.8	16.5	14.6	13.2
7				89.5	77.4	64.5	36.6	28.3	23.6	20.4	18.0	16.1
8				96.7	85.4	75.0	63.4	37.5	29.6	25.0	21.8	19.4
9					91.8	82.3	73.1	62.5	38.2	30.6	26.1	23.0
10					97.5	88.2	79.9	71.7	61.8	38.8	31.5	27.2
11						93.3	85.4	78.0	70.4	61.2	39.3	32.3
12						97.9	90.1	83.1	76.4	69.4	60.7	39.8
13							94.3	87.5	81.2	75.0	68.5	60.2
14							98.2	91.5	85.4	79.6	73.9	67.7
15								95.1	89.1	83.5	78.2	72.8
16								98.4	92.5	87.1	82.0	77.0
17									95.6	90.3	85.4	80.6
18									98.6	93.3	88.4	83.9
19										96.1	91.3	86.8
20										98.7	94.0	89.5
21											96.5	92.1
22											98.9	94.5
23												96.8
24												98.9

4.3.1 For circular stacks locate the traverse points on at least two diameters according to figure 104-4 and table 104-1. The traverse axes shall divide the stack cross section into equal parts.

4.3.2 For rectangular stacks divide the cross section into as many equal rectangular areas as traverse points, such that the ratio of the length to the width of the elemental areas is between 1 and 2. Locate the traverse points at the centroid of each equal area according to figure 104-5.

4.4 *Measurement of stack conditions.*—4.4.1 Set up the apparatus as shown in figure 104-2. Make sure all connections are tight and leak free. Measure the velocity head and temperature at the traverse points specified by §§ 4.2 and 4.3.

4.4.2 Measure the static pressure in the stack.

4.4.3 Determine the stack gas moisture.

4.4.4 Determine the stack gas molecular weight from the measured moisture content and knowledge of the expected gas stream composition. A standard Orsat analyzer has been found valuable at combustion sources. In all cases, sound engineering judgment should be used.

4.5 *Preparation of sampling train.*—4.5.1 Prior to assembly, clean all glassware (probe, impingers, and connectors) by soaking in wash acid for 2 hours. Place 100 ml of distilled water in each of the first two impingers, leave the third impinger empty, and place approximately 200 g of preweighted silica gel in the fourth impinger. Save a portion of the distilled water as a blank in the sample analysis. Set up the train and the probe as in figure 104-1.

4.5.2 Leak check the sampling train at the sampling site. The leakage rate should not be in excess of 1 percent of the desired sampling rate. If condensation in the probe or filter is a problem, probe and filter heaters will be required. Adjust the heaters to provide a temperature at or above the stack temperature. However, membrane filters such as the Millipore AA are limited to about 225° F. If the stack gas is in excess of about 200° F., consideration should be given to an alternate procedure such as moving the filter holder downstream of the first impinger to insure that the filter does not exceed its temperature limit. Place crushed ice around the impingers. Add more ice during the test to keep the temperature of the gases leaving the last impinger at 70° F. or less.

4.6 *Beryllium train operation.*—4.6.1 For each run, record the data required on the example sheet shown in figure 104-6. Take readings at each sampling point at least every 5 minutes and when significant changes in stack conditions necessitate additional adjustments in flow rate.

4.6.2 Sample at a rate of 0.5 to 1.0 ft^3/min. Samples shall be taken over such a period or periods as are necessary to accurately determine the maximum emissions which would occur in a 24-hour period. In the case of cyclic operations, sufficient tests shall be made so as to allow accurate determination or calculation of the emissions which will occur over the duration of the cycle. A minimum sample time of 2 hours is recommended.

PLANT_____
LOCATION_____
OPERATOR_____
DATE_____
RUN NO._____
SAMPLE BOX NO._____
METER BOX NO._____
METER $\Delta H_@$_____
C FACTOR_____

SCHEMATIC OF STACK CROSS SECTION

AMBIENT TEMPERATURE_____
BAROMETRIC PRESSURE_____
ASSUMED MOISTURE %_____
HEATER BOX SETTING_____
PROBE LENGTH m._____
NOZZLE DIAMETER, in._____
PROBE HEATER SETTING_____

TRAVERSE POINT NUMBER	SAMPLING TIME (θ) min.	STATIC PRESSURE (P_g) in. Hg.	STACK TEMPERATURE (T_s), °F	VELOCITY HEAD, (ΔP_s),	PRESSURE DIFFERENTIAL ACROSS ORIFICE METER (ΔH), in. H_2O	GAS SAMPLE VOLUME (V_m) ft^3	GAS SAMPLE TEMPERATURE AT DRY GAS METER		SAMPLE BOX TEMPERATURE, °F	IMPINGER TEMPERATURE, °F
							INLET ($T_{m_{in}}$), °F	OUTLET ($T_{m_{out}}$), °F		
TOTAL							Avg	Avg		
AVERAGE							Avg			

Figure 104-6.1 Field data

4.6.3 To begin sampling, position the nozzle at the first traverse point with the tip pointing directly into the gas stream. Immediately start the pump and adjust the flow to isokinetic conditions. Sample for at least 5 minutes at each traverse point; sampling time must be the same for each point. Maintain isokinetic sampling throughout the sampling period. Nomographs which aid in the rapid adjustment of the sampling rate without other computations are in APTD-0576 and are available from commercial suppliers. Note that standard nomographs are applicable only for type S pitot tubes and air or a stack gas with an equivalent density. Contact EPA or the sampling train supplier for instructions when the standard nomograph is not applicable.

4.6.4 Turn off the pump at the conclusion of each run and record the final readings. Immediately remove the probe and nozzle

from the stack and handle in accordance with the sample recovery process described in § 4.7.

4.7 *Sample recovery*—4.7.1 (All glass storage bottles and the graduated cylinder must be precleaned as in § 4.5.1.) This operation should be performed in an area free of possible beryllium contamination. When the sampling train is moved, care must be exercised to prevent breakage and contamination.

4.7.2 Disconnect the probe from the impinger train. Remove the filter and any loose particulate matter from the filter holder and place in a sample bottle. Place the contents (measured to ±1 ml) of the first three impingers into another sample bottle Rinse the probe and all glassware between it and the back half of the third impinger with water and acetone, and add this to the latter sample bottle Clean the probe with a brush or a long slender rod and cotton balls Use acetone while cleaning. Add these to the sample bottle Retain a sample of the water and acetone as a blank. The total amount of wash water and acetone used should be measured for accurate blank correction. Place the silica gel in the plastic jar. Seal and secure all sample containers for shipment If an additional test is desired, the glassware can be carefully double rinsed with distilled water and reassembled. However, if the glassware is to be out of use more than 2 days, the initial acid wash procedure must be followed.

4.8 Analysis.

4.8.1 *Apparatus preparation*—Clean all glassware according to the procedure of section 4.5.1. Adjust the instrument settings according to the instrument manual, using an absorption wavelength of 234.8 nm.

4.8.2 *Sample preparation*—The digestion of beryllium samples is accomplished in part in concentrated perchloric acid. *Caution*: The analyst must insure that the sample is heated to light brown fumes after the initial nitric acid addition; otherwise, dangerous perchlorates may result from the subsequent perchloric acid digestion Perchloric acid also should be used only under a perchloric acid hood.

4.8.2.1 Transfer the filter and any loose particulate matter from the sample container to a 150 ml beaker. Add 35 ml concentrated nitric acid. Heat on a hotplate until light brown fumes are evident to destroy all organic matter Cool to room temperature and add 5 ml concentrated sulfuric acid and 5 ml concentrated perchloric acid. Then proceed with step 4.8.2.4.

4.8.2.2 Place a portion of the water and acetone sample into a 150 ml beaker and put on a hotplate. Add portions of the remainder as evaporation proceeds and evaporate to dryness Cool the residue and add 35 ml concentrated nitric acid. Heat on a hotplate until light brown fumes are evident to destroy any organic matter. Cool to room temperature and add 5 ml concentrated sulfuric acid, and 5 ml concentrated perchloric acid. Then proceed with step 4.8.2.4.

4.8.2.3 Weigh the spent silica gel and report to the nearest gram.

4.8.2.4 Samples from 4.8.2.1 and 4.8.2.2 may be combined here for ease of analysis. Replace on a hotplate and evaporate to dryness in a perchloric acid hood. Cool and dissolve the residue in 10.0 ml of 25 percent V/V hydrochloric acid. Samples are now ready for the atomic absorption unit. The beryllium concentration of the sample must be within the calibration range of the unit. If necessary, further dilution of sample with 25 percent V/V hydrochloric acid must be performed to bring the sample within the calibration range.

4.8.3 *Beryllium determination*.—Analyze the samples prepared in 4.8.2 at 234.8 nm using a nitrous oxide/acetylene flame. Aluminum, silicon and other elements can interfere with this method if present in large quantities Standard methods are available, however, to effectively eliminate these interferences (see Reference 5).

5. *Calibration*—5.1 *Sampling train*.—5.1.1 Use standard methods and equipment as detailed in APTD-0576 to calibrate the rate meter, pitot tube, dry gas meter and probe heater (if used). Recalibrate prior to each test series

5.2 *Analysis*.—5.2.1 Standardization is made with the procedure as suggested by the manufacturer with standard beryllium solution. Standard solutions will be prepared from the stock solution by dilution with 25 percent V/V hydrochloric acid. The linearity of working range should be established with a series of standard solutions. If collected samples are out of the linear range, the samples should be diluted. Standards should be interspersed with the samples since the calibration can change slightly with time.

6 *Calculations* 6.1 *Average dry gas meter temperature, stack temperature, stack pressure and average orifice pressure drop*.—See data sheet (figure 104-6).

6.2 *Dry gas volume*.—Correct the sample volume measured by the dry gas meter to stack conditions by using equation 104-2.

$$V_{m_s} = V_m \frac{T_s}{T_m} \frac{\left(P_{bar} + \frac{\Delta H}{13.6}\right)}{P_s} \qquad \text{eq. 104-2}$$

where:

V_{m_s} = Volume of gas sample through the dry gas meter (stack conditions), ft³.

V_m = Volume of gas sample through the dry gas meter (meter conditions), ft³.

T_s = Average temperature of stack gas, °R.

T_m = Average dry gas meter temperature, °R.

P_{bar} = Barometric pressure at the orifice meter, in Hg.

ΔH = Average pressure drop across the orifice meter, in H_2O.

13.6 = Specific gravity of mercury.

P_s = Stack pressure, $P_{bar} \pm$ static pressure, in Hg.

6.3 *Volume of water vapor*.

$$W_{v_s} = K_w V_{l_c} \frac{T_s}{P_s} \qquad \text{eq. 104-3}$$

where:

V_{w_s} = Volume of water vapor in the gas sample (stack conditions), ft³.

K_w = 0.00267 $\frac{\text{in Hg-ft}^3}{\text{ml-°R}}$, when these units are used.

V_{l_c} = Total volume of liquid collected in impingers and silica gel (see figure 104-7), ml.

T_s = Average stack gas temperature, °R.

P_s = Stack pressure, $P_{bar} \pm$ static pressure, in Hg.

6.4 *Total gas volume*.

$$V_{total} = V_{m_s} + V_{w_s} \qquad \text{eq. 104-4}$$

where

V_{total} = Total volume of gas sample (stack conditions), ft³.

V_{m_s} = Volume of gas through dry gas meter (stack conditions), ft³.

V_{w_s} = Volume of water vapor in gas sample (stack conditions), ft³.

6.5 *Stack gas velocity*.

Use equation 104-5 to calculate the stack gas velocity.

$$(v_s)_{avg.} = K_p C_p (\sqrt{\Delta p})_{avg.} \sqrt{\frac{(T_s)_{avg.}}{P_s M_s}} \qquad \text{eq. 104-5}$$

where:

$(v_s)_{avg.}$ = Average stack gas velocity, feet per second.

K_p = 85.53 $\frac{\text{ft}}{\text{sec}} \left(\frac{\text{lb-in Hg}}{\text{lb mole-°R-in H}_2\text{O}}\right)^{1/2}$, when these units are used.

C_p = Pitot tube coefficient, dimensionless.

$(T_s)_{avg.}$ = Average stack gas temperature, °R.

$(\sqrt{\Delta p})_{avg.}$ = Average square root of the velocity head of stack gas $(\text{in H}_2\text{O})^{1/2}$ (see figure 104-6).

P_s = Stack pressure, $P_{bar} \pm$ static pressure, in Hg.

M_s = Molecular weight of stack gas (wet basis)- the summation of the products of the molecular weight of each component multiplied by its volumetric proportion in the mixture, lb/lb-mole.

	VOLUME OF LIQUID WATER COLLECTED	
	IMPINGER VOLUME, ml	SILICA GEL WEIGHT, g
FINAL		
INITIAL		
LIQUID COLLECTED		
TOTAL VOLUME COLLECTED		g* ml

*CONVERT WEIGHT OF WATER TO VOLUME BY dividing total weight INCREASE BY DENSITY OF WATER. (1 g/ml):

$$\frac{\text{INCREASE, g}}{(1\ \text{g/ml})} = \text{VOLUME, WATER, ml}$$

Figure 104-7. Analytical data.

PLANT_____

DATE_____

RUN NO._____

STACK DIAMETER, in._____

BAROMETRIC PRESSURE, in. Hg._____

STATIC PRESSURE IN STACK (P_g), in. Hg._____

OPERATORS_____

SCHEMATIC OF STACK CROSS SECTION

Traverse point number	Velocity head, in. H_2O	$\sqrt{\Delta_p}$	Stack Temperature (T_S), °F
AVERAGE:			

Figure 104-8. Velocity traverse data.

Figure 104–8 shows a sample recording sheet for velocity traverse data. Use the averages in the last two columns of figure 104–8 to determine the average stack gas velocity from equation 104–5

6 6 *Beryllium collected*.—Calculate the total weight of beryllium collected by using equation 104–6

$$W_t = V_t C_t - V_w C_w - V_a C_a \quad \text{eq 104–6}$$

where:

W_t = Total weight of beryllium collected, μg.

V_t = Total volume of hydrochloric acid from step 4 8 2.4, ml.

C_t = Concentration of beryllium found in sample, μg/ml.

V_w = Total volume of water used in sampling (impinger contents plus all wash amounts), ml.

C_w = Blank concentration of beryllium in water, μg/ml.

V_a = Total volume of acetone used in sampling (all wash amounts), ml.

C_a = Blank concentration of beryllium in acetone, μg/ml.

6 7 *Total beryllium emissions*.—Calculate the total amount of beryllium emitted from each stack per day by equation 104–7. This equation is applicable for continuous operations For cyclic operations, use only the time per day each stack is in operation. The total beryllium emissions from a source will be the summation of results from all stacks.

$$R = \frac{W_t (v_s)_{avg} A_s}{V_{total}} \times \frac{86{,}400 \text{ seconds/day}}{10^6 \text{ μg/g}} \quad \text{eq. 104–7}$$

where

R = Rate of emission, g/day.

W_t = Total weight of beryllium collected, μg.

V_{total} = Total volume of gas sample (stack conditions), ft³

$(v_s)_{avg}$ = Average stack gas velocity, feet per second.

A_s = Stack area, ft².

6 8 *Isokinetic variation (comparison of velocity of gas in probe tip to stack velocity)*.

$$I = \frac{100 V_{total}}{A_n \Theta (v_s)_{avg}} \quad \text{eq. 104–8}$$

where.

I = Percent of isokinetic sampling.

V_{total} = Total volume of gas sample (stack conditions), ft³

A_n = Probe tip area, ft².

Θ = Sampling time, sec.

$(v_s)_{avg}$ = Average stack gas velocity, feet per second.

7. *Evaluation of results*—7 1 *Determination of compliance*—7.1 1 Each performance test shall consist of three repetitions of the applicable test method. For the purpose of determining compliance with an applicable national emission standard, the average of results of all repetitions shall apply.

7.2 *Acceptable isokinetic results*—7.2 1 The following range sets the limit on acceptable isokinetic sampling results:

If 90 percent $\leq I \leq$ 110 percent, the results are acceptable; otherwise, reject the test and repeat.

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APPENDIX B

MRI'S FIELD LOG

A. General Equipment

Collaborator 1

RAC console

RAC sample box

RAC probe

Rubber vacuum hose

No stack temperature

Using ~ 2-1/2-in. millipore type filter

Using 0.25 in. ID probe tip

Heat on filter compartment (~ 150°)

Heat on probe (~ 50°).

Collaborator 2

RAC console

RAC sample box

RAC probe

Stack thermocouple and pot used for stack temperature but not at every point

Using ~ 90 mm millipore type filter with Whatman No. 41 backup

Using 0.375 in. ID probe tip

No heat used on filter compartment

Heat (~ 30°) used on probe.

Collaborator 3

RAC console

RAC sample box

RAC probe (MRI)

Rubber vacuum hose

Bimetallic thermometer used for stack temperature--not at each sample point

Using ~ 2-1/2 in. millipore filter

Using 0.375 in. ID probe tip

Using heat on filter box (~ 220°)

Heat on probe (~ 60°).

Collaborator 4

RAC console

RAC sample box

RAC probe

Poly vacuum hose and Pitot tubes

0-0.25 in. inclined manometer used instead of console manometer for stack

Bimetallic thermometer in ports used for stack temperature--not at each sampling point

Using ~ 90 mm millipore type filter with Whatman No. 41 backup

Using 0.304 in. ID probe tip

No heat used for filter compartment

No heat used for probe.

B. General Observations

4 December 1973 Run No. 1

Test start	1125
stop	1545
MRI on-site	0800
Collaborator 1	0830
Collaborator 2	0830
Collaborator 3	1000
Collaborator 4	0830

Test started late due to lack of power; had to rig extension cords to interior of building.

Collaborator 1 changed probe tips at end of first port. Went to 1/4 in. as could not maintain isokinetic.

Collaborator 2 lost vacuum and thought filter broke. Releak checked. No problem. Lost ~ 4 min. Made up during first port change.

Weather: clear, cold, windy. High in Denver: 37°.

5 December 1973 Run No. 2

Test start	1000
stop	1415
MRI on-site	0800
Collaborator 1	0930
Collaborator 2	0830
Collaborator 3	0900
Collaborator 4	0900

Collaborator 1 had checked pump and filter to try to alleviate problems. It was drawing 15 Hg through clean filter.

Collaborator 1, no vacuum during first port. Releak checked. Si gel impinger and filter holder loose. Fixed during port change.

Weather: clear, cold, windy. High in Denver: 38°.

6 December 1973 Run No. 3

Test start	0930
stop	1345
MRI on-site	0800
Collaborator 1	0900
Collaborator 2	0830
Collaborator 3	0900
Collaborator 4	0830

Collaborator 1, changed console pumps between Runs 2 and 3. New pump much better.

There was no problem in maintaining isokinetic and much better vacuum readings were obtained. No problems with test. Some pumps were slow in starting which was possibly due to cold.

Weather: clear, cold, windy. High in Denver: 43°.

7 December 1973 Run No. 4

Test start	0910
stop	1330
MRI on-site	0800
Collaborator 1	0845
Collaborator 2	0845
Collaborator 3	0830
Collaborator 4	0830

Collaborator 3, first impinger and U-tube broken during third port change. Replaced on-site. Continued test.

Collaborator 2, probe broken during fourth port change. There appeared to be no air leak so finished test.

Weather: cool, partly cloudy, moderate wind. High in Denver: ~ 50°.

10 December 1973 Run No. 5

Test start	0915
stop	1330
MRI on-site	0800
Collaborator 1	0845
Collaborator 2	0830
Collaborator 3	0830
Collaborator 4	0845

Collaborator 1's pump vanes stuck and pump inoperative at start of test. Started 16 min (2 points) behind others. Made up during port change (No. 1).

Collaborator 1 broke probe during port change No. 2. Rails dropped off while extracting probe following port test. Called office and new liner brought immediately to site. Ran without probe heat. Held all testing about 30 min until probe liner was exchanged.

Collaborator 1 reported that liquid portion of sample for Run 4 was lost to accidental spillage. No confirmation.

Fixed rails to prevent slippage and probe breakage.

Weather: partly cloudy, moderate wind, warm. High in Denver: 60°.

11 December 1973 Run No. 6

Test start	0910
stop	1320
MRI on-site	0800
Collaborator 1	0830
Collaborator 2	0830
Collaborator 3	0830
Collaborator 4	0830

No major problems. Collaborator 1 again had pump starting problems but cleared up.

Collaborator 2 thought to have leak but fixed prior to testing.

Weather: partly cloudy, moderate wind, cool. High in Denver: 56°.

12 December 1973 Run No. 7

Test start	1215
stop	1635
MRI on-site	0810
Collaborator 1	0830
Collaborator 2	0900 (late due to high winds closing road)
Collaborator 3	0800
Collaborator 4	0830

Weather bad in a.m. Winds gusting to ~ 60-75 mph. Conditions considered unsafe for personnel on stack. Decision made to review conditions at 1130 as to go or no-go for 12 December. Situation improved by 1130. Winds to 40-50 mph but slackening. Considered by all okay for sampling. Some heavy gusts but general abatement during sampling period. No worse than usual by 1530.

Collaborator 4 had trouble with pitot lines. At first thought to be result of turbulence in stack from high west and northwest winds but did not improve after port change. Other three teams pitot readings okay. Collaborator 4 shutdown and replaced downstream line with Tygon. Time made up during port change. Readings okay.

Weather: clear, cool, very windy. High in Denver: 50°.

13 December 1973 Run No. 8

Test start	0915
stop	1325
MRI on-site	0820
Collaborator 1	0845
Collaborator 2	0830
Collaborator 3	0845
Collaborator 4	0845

No problems.

Weather: warm, partly cloudy, little wind. High in Denver: 53°.

14 December 1973 Run No. 9

Test start	0920
stop	1330
MRI on-site	0820
Collaborator 1	0830
Collaborator 2	0845
Collaborator 3	0830
Collaborator 4	0900

No problems

Weather: clear, cool, moderate wind. High in Denver: 47°.

17 December 1973 Run No. 10

Test start	0900
stop	1335
MRI on-site	0815
Collaborator 1	0830
Collaborator 2	0830
Collaborator 3	0830
Collaborator 4	0830

Collaborator 2's filter got wet during leak check, which created too great a vacuum such that isokinetic sampling could not be achieved. Filter replaced and three points picked up at conclusion of test.

No other problems.

Weather: cloudy, warm, light wind. High in Denver: 63°.

18 December 1973 No Test

No test

MRI on-site	0800
Collaborator 1	0845
Collaborator 2	0845
Collaborator 3	0800
Collaborator 4	0830

Began snowing ~ 0715. Decision made to start test as only snow, no wind and 19 December to be worse. Set up and ready to go by 1010 when wind came up. Scaffold became icy and visibility poor. Decided not to begin test. Conditions worsened during lowering of equipment, wind increasing.

19 December 1973 Run No. 11

Test start	0930
stop	1345
MRI on-site	0830
Collaborator 1	0900
Collaborator 2	0900
Collaborator 3	0830
Collaborator 4	0845

Collaborator 4 experienced rapid rise in vacuum during first port. Thought to be wet filter. Filter replaced--not wet. Most likely source--water freezing in S-g nozzle or frozen check valve. Lost 3 min. Made up at end of port.

No further problems.

Weather: cold, partly cloudy, no wind. High in Denver: 24°.

20 December 1973 Run No. 12

Test start	0915
stop	1330
MRI on-site	0830
Collaborator 1	0830
Collaborator 2	0845
Collaborator 3	0830
Collaborator 4	0845

Collaborator 2 changed probe tips following first port. Could not maintain isokinetic.

Weather: cold, clear, little wind. High in Denver: 44°.

21 December 1973 Run No. 13

Test start	0905
stop	1320
MRI on-site	0830
Collaborator 1	0845
Collaborator 2	0830
Collaborator 3	0815
Collaborator 4	0830

Collaborator 1 had large vacuum on first port. Stopped and reversed filter. Okay. Made up time at port change.

Weather: cool, partly cloudy, moderate wind. High in Denver: ~ 50°.

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1 REPORT NO EPA-650/4-74-023	2
3 RECIPIENT'S ACCESSION NO	
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7 AUTHOR(S) P. C. Constant, Jr. and M. C. Sharp	8 PERFORMING ORGANIZATION REPORT NO
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16 ABSTRACT

A collaborative test of EPA Method 104 for beryllium was conducted at the Coors Porcelain Company in Golden, Colorado during the period of December 4-21, 1973. The test comprised 13 runs, each on a different day, where four different collaborative organizations sampled simultaneously over the same 30 point traverse in the stack, with each point being sampled 8 minutes by each collaborator. In addition, the collaborators analyzed simulated standard samples prepared by the National Bureau of Standards.

A statistical analysis of the data provides estimates of the variance of repeated observations per collaborator, the variance between collaborators and the accuracy of the method.

17 KEY WORDS AND DOCUMENT ANALYSIS

a DESCRIPTORS	b IDENTIFIERS/OPEN ENDED TERMS	c COSATI Field/Group
Air pollution Beryllium Data Experimental design Statistical analysis Exhaust emissions	Open ended Collatorative test EPA Method 104 Stationary sources Ceramic manufacturer or plant	13B 7B

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