LBL-9128 c.2
UC-38

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

Engineering & Technical Services Division

BETA-GAUGE METHODS APPLIED TO AEROSOL SAMPLES

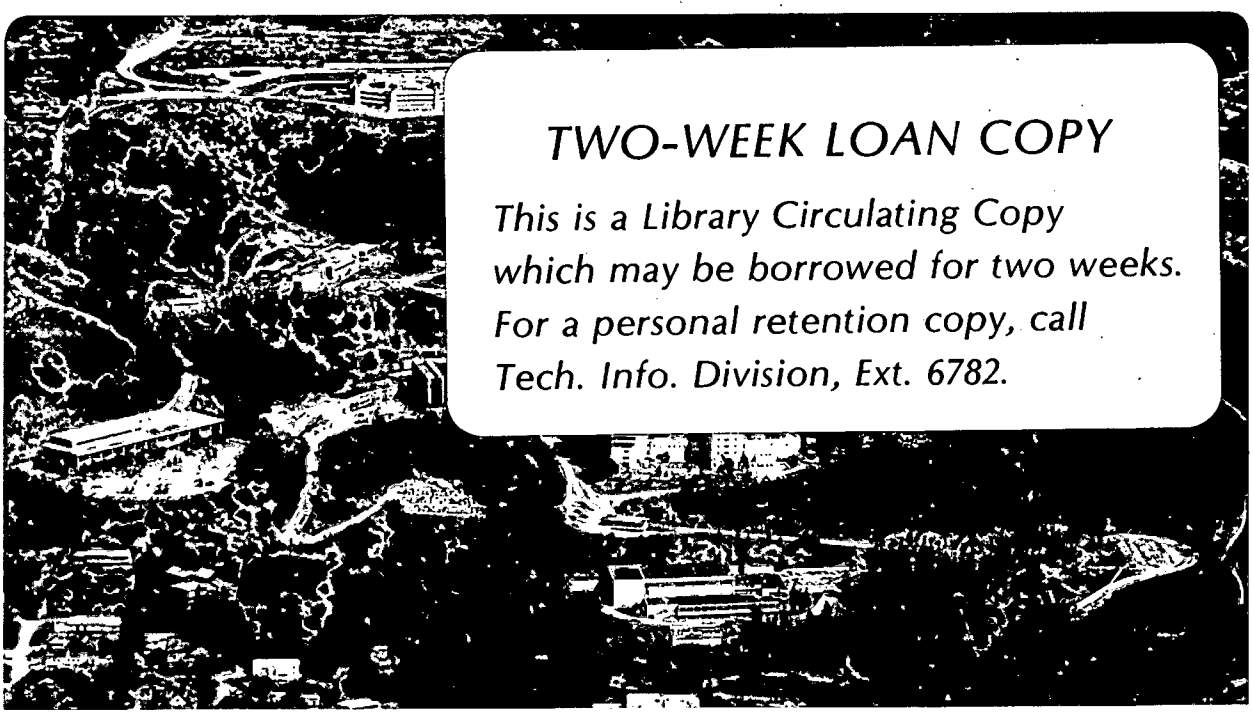
RECEIVED
LAWRENCE
BERKELEY LABORATORY

MAR 14 1980

LIBRARY AND
DOCUMENTS SECTION

J. M. Jaklevic, R. C. Gatti, F. S. Goulding,
and B. W. Loo

November 1979



TWO-WEEK LOAN COPY

This is a Library Circulating Copy which may be borrowed for two weeks. For a personal retention copy, call Tech. Info. Division, Ext. 6782.

LBL 9128 c.2

Prepared for the U.S. Department of Energy under Contract W-7405-ENG-48

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

LBL-9128
November, 1979

BETA-GAUGE METHODS APPLIED TO AEROSOL SAMPLES

by

J. M. Jaklevic, R. C. Gatti,
F. S. Goulding, and B. W. Loo
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720 U.S.A.

Interagency Agreement No. EPA-IAG-D8-E681-CG, 8DBCG

Project Officer

Thomas G. Dzubay
Atmospheric Chemistry and Physics Division
Environmental Sciences Research Laboratory
Research Triangle Park, N. C. 27711

Prepared for the U. S. Department of Energy
under Contract No. W-7405-ENG-48
and for the Environmental Protection Agency

ENVIRONMENTAL SCIENCES RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, N. C. 27711

DISCLAIMER

This report has been reviewed by the Environmental Sciences Research Laboratory, U. S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the U. S. Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the Department of Energy or the Environmental Protection Agency, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

This report was done with support under the interagency agreement with the Department of Energy and Environmental Protecton Agency. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy, nor does mention of trade names or commerical products constitute endorsement or recommendation for use.

ABSTRACT

An instrument for the routine measurement of aerosol mass using the beta-particle attenuation method is described. Factors affecting the precision and accuracy of the measurement are discussed in detail. Results of inter-comparison studies between the beta gauge method and conventional gravimetric are presented. The design of the present instrument is particularly well suited for the automatic analysis of membrane filter obtained from modern dichotomous samplers.

This report was submitted in fulfillment of Contract No. EPA-IAG-D8-E681-CG, 80 BCG by the Lawrence Berkeley Laboratory under the sponsorship of the U. S. Environmental Protection Agency. This report covers the period August 28, 1978 to August 28, 1979.

CONTENTS

Abstract iii

Figures. v

Tables vi

Acknowledgements vii

1. Introduction 1

2. Description of Method. 2

3. Description of Instrument. 10

4. Precision and Accuracy 13

Precision. 14
Accuracy 15
Particle Size and Filter Inhomogeneity 16
Atomic Number Dependence 19

5. Results And Summary 24

References 28

FIGURES

Number		Page
1.	Schematic of a beta-gauge suitable for measuring thin aerosol samples.	3
2.	Idealized beta-particle spectrum emitted from a radioisotope source.	5
3.	Range-energy curves for monoenergetic electrons with energies in the region appropriate for beta-thickness gauges. Curves are shown for a) lead, b) copper, and c) carbon.	6
4.	Attenuation curves for thin polycarbonate films using two radioisotopes a) ^{14}C, and b) ^{147}Pm.	8
5.	Automatic sample handling and data acquisition system used in conjunction with the beta-gauge.	11
6.	The discrepancy in beta-gauge mass measurements as a function of particle size for the case of two commonly used isotopes.	18
7.	Measured values for the mass absorption coefficients as a function of atomic number and atomic mass.	21
8.	Comparison of beta-gauge results with those obtained by gravimetric methods. These data were obtained by comparing side-by-side samples of the same atmospheric aerosol collected by different samplers. Case A represents high volume samples vs. dichotomous. Case B was obtained with manual dichotomous vs. automatic dichotomous samplers.	25
9.	Comparison of beta-gauge results with those obtained by gravimetric methods. These data represent duplicate mass measurements on the same sample. Samples for curve A were obtained in our laboratory. The data shown in curve B were obtained from workers at EPA[13].	26

TABLES

Number		Page
1	Commonly Available Sources Suitable for Beta Attenuation Measurements	2
2	Stability Tests for Room Temperature Beta-Gauge Measurements Represent Precision in the Calibration Parameters and Calculated Masses Which Were Observed in the Repeated Measurement of Fine Thin-Film Standards	16
3	Measured Mass Absorption Coefficients for Substances with Varying Effective Atomic Number and Mass	20
4	Effect of Atomic Number Dependence on the Measured Mass of Several Compounds. Column Four Gives the Discrepancy with Respect to the Polycarbonate Standards	23

ACKNOWLEDGEMENTS

The authors would like to acknowledge the support of several other members of the Department of Instrument Techniques including D. Landis, D. Adachi and N. Madden who assisted in the detector and electronic development, and W. Searles who did much of the mechanical design. We have profited from discussions with T. Dzubay of the United States Environmental Protection Agency and W. Courtney of Northrup Services, Inc.

SECTION 1

INTRODUCTION

The beta-gauge method of mass measurement is based on the attenuation which a beta-particle spectrum undergoes when traversing a thin film of matter. If one measures the total number of electrons in a continuous beta-particle spectrum emanating from a radioisotope source, the number of electrons transmitted through a thin, uniform foil would be [1,2]

$$I = I_0 e^{-\mu x} \qquad (1)$$

where I_0 is the incident flux, μ is the mass absorption coefficient in cm^2/g and x is the thickness of the film expressed in g/cm^2. If μ and I_0 are accurately known, then a measurement of I can be directly related to the mass of a given sample. The values of μ and I_0 are normally determined by measuring I as a function of x for several known standards.

Beta thickness gauges based on the above model have been used for several years in applications where continuous, non-destructive monitoring of thin films is required, for example, in certain industrial processes.[3,4] Several authors have recently applied the method to the measurement of particulate deposits collected from the atmospheric aerosol.[5,6,7] The use of the beta-gauge method has several potential advantages over direct weighings for the measurements of aerosol samples. Handling of the fragile filter samples is minimized, the risk of contamination is reduced, and the automated analysis of many samples can be facilitated. Insofar as a beta-gauge can be made to operate with a precision and accuracy comparable to current microbalance technology, it represents a preferred approach in modern, large-scale monitoring programs.

The measurement of the aerosol particulate deposits collected on filter substrates represents a particularly demanding mass measurement problem. Modern air sampling techniques result in typical particulate deposits of 50 to 200 $\mu g/cm^2$ on filter subtrates weighing 1 to 5 mg/cm^2. Variations in substrate mass from sample to sample require that each filter be weighed before and after exposure. A precision of ± 5 $\mu g/cm^2$ in the measurement of the aerosol deposit requires a maximum error of ± 3 $\mu g/cm^2$ in each individual weighing. A direct measurement on a 5 mg/cm^2 substrate therefore requires a precision of ± 0.06%. The calibration accuracy must be assured in the presence of potential particle size, filter non-uniformity effects and additional artifacts unique to the beta particle attentuation method. In order to achieve the desired performance, it is important that a thorough understanding of the technique and its implications be achieved.

SECTION 2

DESCRIPTION OF METHOD

A schematic of a simple beta-gauge is shown in Figure 1. It consists of a radioactive source, detector and sample. The source is chosen such that beta-particle emission is the predominant mode of decay. The half-life should be sufficiently long that decay corrections over the duration of a measurement cycle are avoided and frequent replacement of the source is not required. Table 1 is a partial list of beta-decay sources which are of use in beta-gauge measurements. Many of these sources are better suited for measurement of thicker samples than those involved in aerosol analysis. The most appropriate choices for thin specimens are ^{14}C, ^{147}Pm, and possibly ^{63}Ni.

TABLE 1 COMMONLY AVAILABLE SOURCES SUITABLE FOR BETA ATTENUATION MEASUREMENTS.

Isotope	Half-Life (years)	E_{max} (meV)	Range in Carbon at E_{max} (mg/cm^2)	Range in Carbon at $E_{aver.} = 0.4\ E_{max}$ (mg/cm^2)
^{63}Ni	92	0.067	7.7	1.6
^{14}C	5730	0.156	32	6.6
^{147}Pm	2.62	0.225	60	13
^{85}Kr	10.76	0.67	290	77
^{36}Cl	3.1×10^4	0.712	320	84
^{204}Tl	3.8	0.765	340	94

The detector and associated electronics must be sensitive to electrons in the energy region of interest and be capable of counting discrete events at a high enough rate to facilitate rapid measurements. Most modern applications employ solid-state semiconductor detectors. These devices measure the

total ionization produced by an incident particle within the sensitive volume of a semiconductor crystal, typically silicon. The output pulses are amplified and a discriminator circuit used to register the detection of electrons with energies above a certain lower limit. Other possible detectors include Geiger tubes and proportional counters.

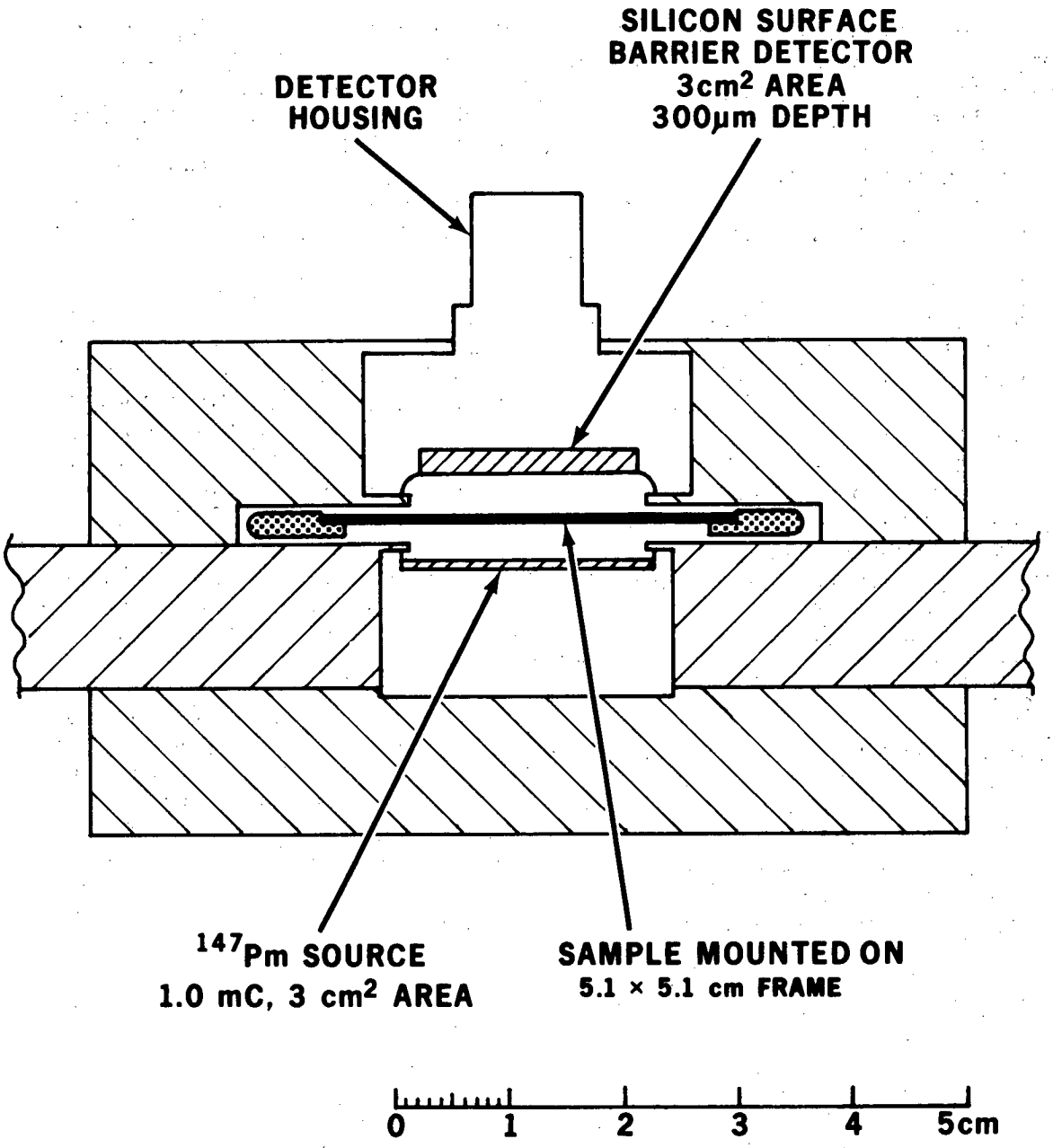


Figure 1. Schematic of a beta-gauge suitable for measuring thin aerosol samples.

The sample is inserted between source and detector and the counts accumulated in the scaler are recorded over some fixed counting interval. The fact that the measurement depends only on the transmission of the particles through the sample itself allows one to mount the filter sample in relatively massive frames without affecting the sensitivity or accuracy. A mechanical system for manipulating these frames can then be used. The automated sample handling represents one of the most important advantages of the beta-gauge method of measurement.

In order to choose a radioactive source for a particular application, the physical processes involved in the measurement should be considered. Figure 2 shows an idealized beta-particle spectrum as emitted from the source. It consists of a continuous energy distribution with an endpoint E_{max} which is characteristic of the isotope used. The maximum number of electrons in the distribution occurs at $E \sim 0.4\ E_{max}$. We have indicated a discrimination level E_{disc} below which the detector and electronics are not sensitive to events; the shaded area represents the measured intensity I.

When traversing the sample material between source and detector, the individual electrons lose energy in a continuous manner via collisions with the electrons in the sample. Their energy and direction are both affected by repeated small energy losses. As the sample thickness is increased, the spectrum of Figure 2 is not uniformly attenuated in terms of the number of particles per unit energy but, instead, undergoes a shift to lower energies accompanied by complete stopping of the lowest energy particles. The measurement then consists of counting the number of electrons with energies remaining above the value E_{disc} after traversing the sample thickness. The exponential dependence given in Equation 1 then results from the fortuitous combination of beta-spectral shape and energy loss behavior of low-energy electrons. It is expected that the exponential behavior will be only approximate for large dynamic ranges of mass.

The choice of a radioactive beta-particle source depends on matching the average energy of the beta-spectrum to the range of mass thickness to be measured. If the electrons in the spectrum have a maximum range which is less than the thickness to be measured, very few electrons will penetrate the sample and the relationship of Equation 1 is no longer valid. Similarly, if the electrons are extremely energetic relative to any losses in a thin sample, then little or no effect will be observed on the spectrum and a sensitive measurement of mass is not possible.

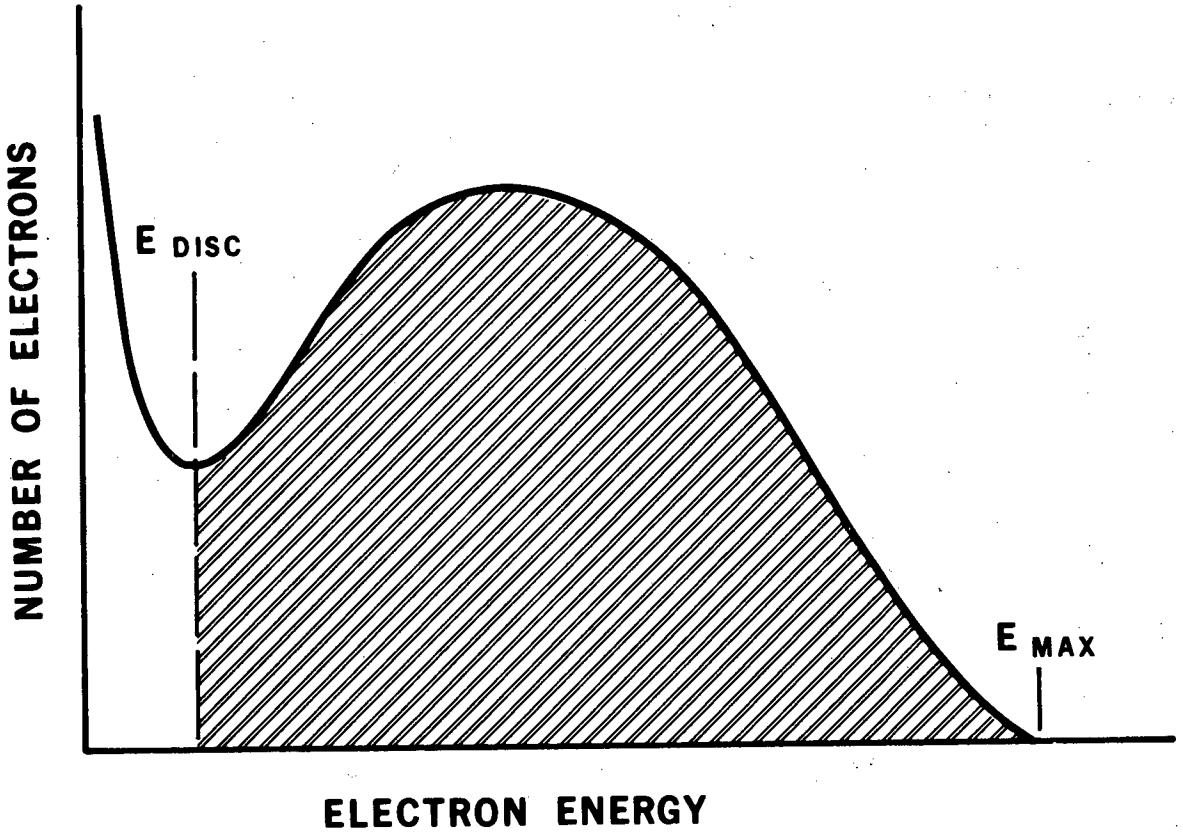


Figure 2. Idealized beta-particle spectrum emitted from a radioisotope source.

Figure 3 shows a curve of the maximum range of electrons in carbon, copper, and lead as a function of energy.[8] Of most importance for the present discussion are the range curves for carbon since most filter substrates consist of hydrocarbon materials. Curves for the other elements are presented in order to show the atomic number dependence and alert us to possible effects which this might have on the mass measurement. Indicated on the plots are the average and endpoint energies for the electron distributions from the commonly employed isotopes ^{14}C and ^{147}Pm. Either of these isotopes is seen to be a practical source for measurement in the 1 mg/cm^2 to 10 mg/cm^2 ranges.

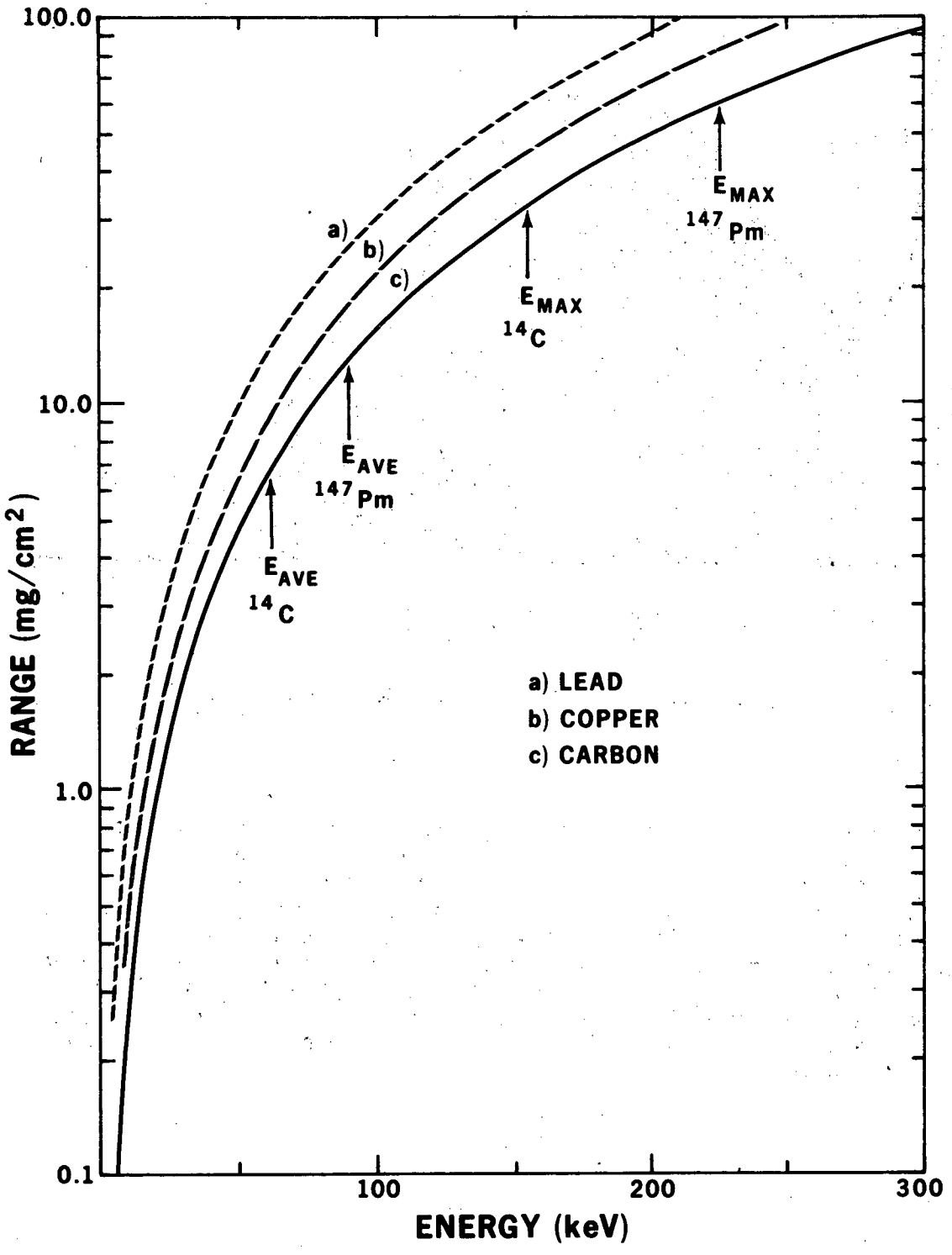


Figure 3. Range-energy curves for monoenergetic electrons with energies in the region appropriate for beta-thickness gauges. Curves are shown for a) lead, b) copper, and c) carbon.

Of more direct concern in the design of a beta-gauge is the relative intensity versus mass thickness described in Equation 1. Figure 4 shows plots of experimental curves for ^{14}C and ^{147}Pm. These were obtained by measuring the variation in counting rates as a function of mass for a series of thin uniform films whose masses were gravimetrically determined. The dashed straight lines represent semi-empirical values calculated from a relationship derived by Gleason et al[2]

$$\mu\ (cm^2/mg) = 0.017\ E_{max}^{-1.43} \qquad (2)$$

where E_{max} is the endpoint energy in MeV. This expression was deduced by measuring the mass absorption coefficient for a number of isotopes with E_{max} ranging from 0.15 to 3.5 MeV and is valid for mass ranges which are small compared to the average electron range. This is consistent with the results shown in Figure 4 where the theoretical slopes are tangent to the experimental result at low mass values.

Based on the results shown, one would conclude that ^{14}C is the best choice for the range of 5 mg/cm^2 or less since the change of counting rates with mass is greater resulting in a higher sensitivity. The ^{147}Pm source has a lower rate of attenuation and is thus better suited to cover a larger mass range. However, since the difference in sensitivity between the two sources is small, the use of ^{147}Pm is often preferred because of the broader range of masses over which it is sensitive. This allows the use of additional protective windows on source and detector. Furthermore, the measurements are less susceptible to artifacts arising from particle size and filter non-uniformity affects.

A close examination of the experimental curves shows that they are not purely exponential over the wide range of masses shown. However, over a relatively narrow range, a reasonable approximation can be maintained. For these reasons, the calibration curve is normally derived from a very limited range which overlaps the range of mass measurement to be made. Assuming a typical deposit to be 200 μg/cm^2 and a root mean square deviation in tare weight of ± 500 μg/cm^2, a calibration range of ± 1 mg/cm^2 is adequate.

In normal operation, the system can be frequently calibrated in order to minimize the effect of long term drift. Our current procedure employs five uniform thin polycarbonate standards which span the mass range of interest. The masses of these standards are first determined by weighing. They are then processed through the beta-gauge and a least squares fit to Equation 1 is performed to obtain I_0 and μ. In general, deviations from a straight line can be observed due to slight inaccuracies (± 10 μg/cm^2) in the gravimetric mass measurement. After repeated measurement in the beta-gauge, the mass values for the thin film standards are corrected to fit a straight line within a typical precision of ± 2 μg/cm^2. The procedure whereby the gravimetric masses are adjusted to conform to the result obtained in the beta-gauge has little effect on the accuracy of the measurement since it involves only a slight correction to the observed slope. In effect, the accuracy of the calibration standards is determined by the average gravimetric mass. Slight systematic variations of the individual

samples are adjusted according to the higher precision afforded by repeated beta-gauge measurements.

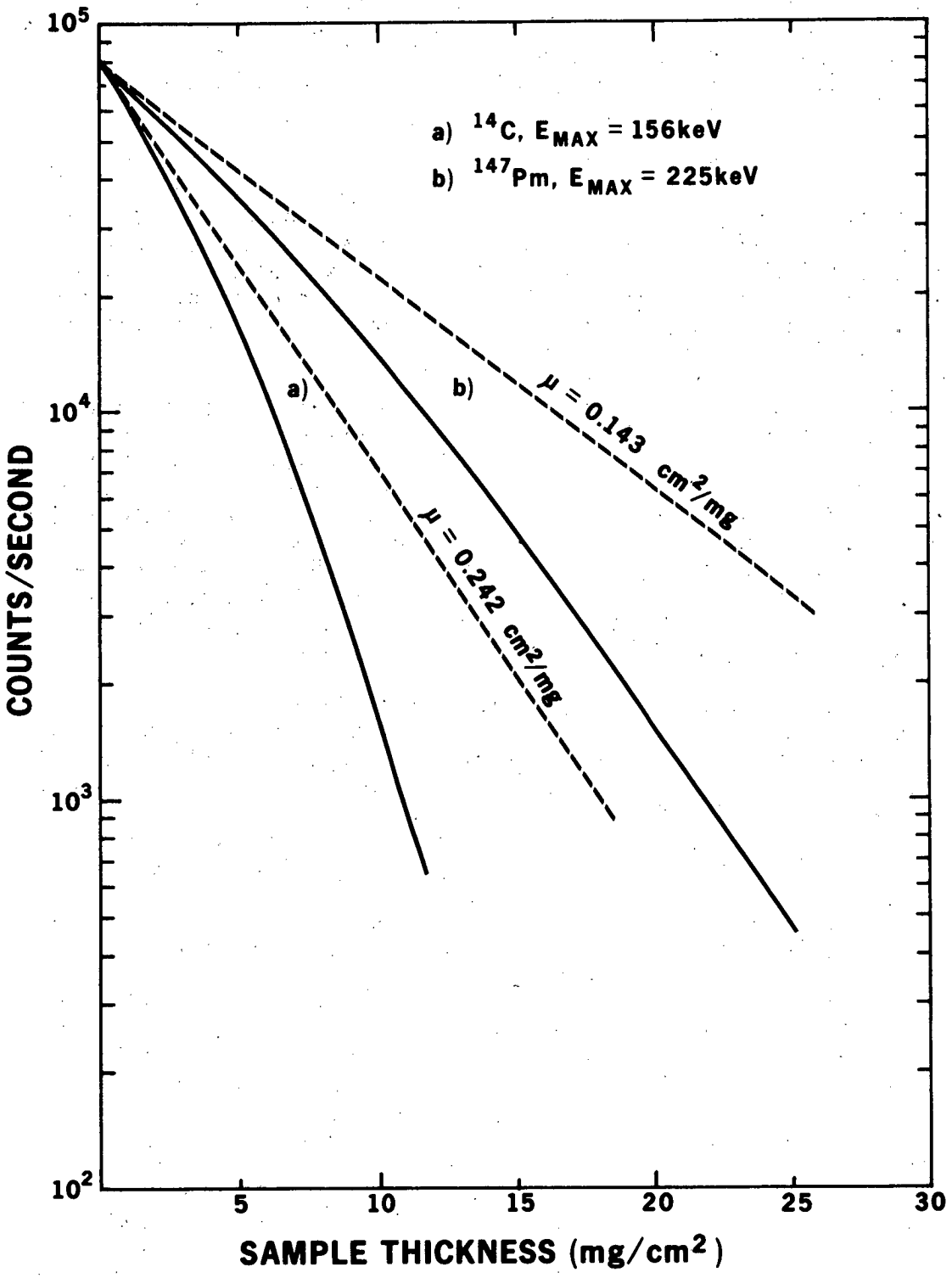


Figure 4. Attenuation curves for thin polycarbonate films using two radioisotopes a) ^{14}C, and b) ^{147}Pm.

Subsequent mass determinations are made by using the μ and I_0 values obtained from the least squares fit in order to calculate the mass from the observed counting rate. The expression is:

$$x = \frac{\ln I_0 - \ln I}{\mu} \tag{3}$$

SECTION 3

DESCRIPTION OF INSTRUMENT

The present approach to mass measurement differs from other beta-gauge procedures[7,9] in that the tare weights are directly calculated relative to calibration standards and stored in that fashion. Although in principle it is possible to store the counts only and compare the counts before and after exposure, the stability of a calibration over a long period of time cannot be guaranteed at the necessary level of precision. Consequently, we require that individual calibration measurements be performed with each measurement. The present beta-gauge design employs a source, sample, and detector geometry similar to that shown in Figure 1. The source is a commercially obtained ^{147}Pm source in a 2.54 cm diameter cylindrical aluminum source holder. The active area is 2.2 cm in diameter and is specified to be uniform to better than ± 10%. The source is protected by a 600 μg/cm^2 foil supplied by the manufacturer; an additional 7 mg/cm^2 Al foil is used to protect the surface of the source from mechanical damage during normal handling and operation.

The detector is an Ortec, Model CA-018-300-300 silicon surface barrier detector operated at room temperature. The active area is 3 cm^2 with a 300 μm (70 mg/cm^2) sensitive depth. The electronic resolution is approximately 12 keV at the operating temperature. The front surface of the detector is also protected by a 7 mg/cm^2 Al foil which reduces the sensitivity of the device to ambient light. The source to detector distance is 0.7 cm representing an air path of approximately 0.7 mg/cm^2 equivalent mass.

Since the present instrument is designed for automatic operation, it is interesting to consider the associated mechanical and electronic hardware. These are illustrated schematically in Figure 5. The sample carrier is designed to accomodate two standard trays with 36 samples each plus an additional five standards at top and bottom. The two trays would typically represent the coarse and fine particle fractions obtained from a dichotomous sampler.[10] The five standards at the bottom are normally used to calculate the thin film calibration constants. The top standards are blank filters of the type used in the study and are employed as cross checks on system stability and calibration accuracy.

The detector preamplifier, amplifier, and discrimination circuitry were designed and built in our laboratory and have been extensively tested for stability. Repeated measurement of the same counting rate over extended periods of time indicate a long term stability in the entire system of one part in 3 x 10^4.

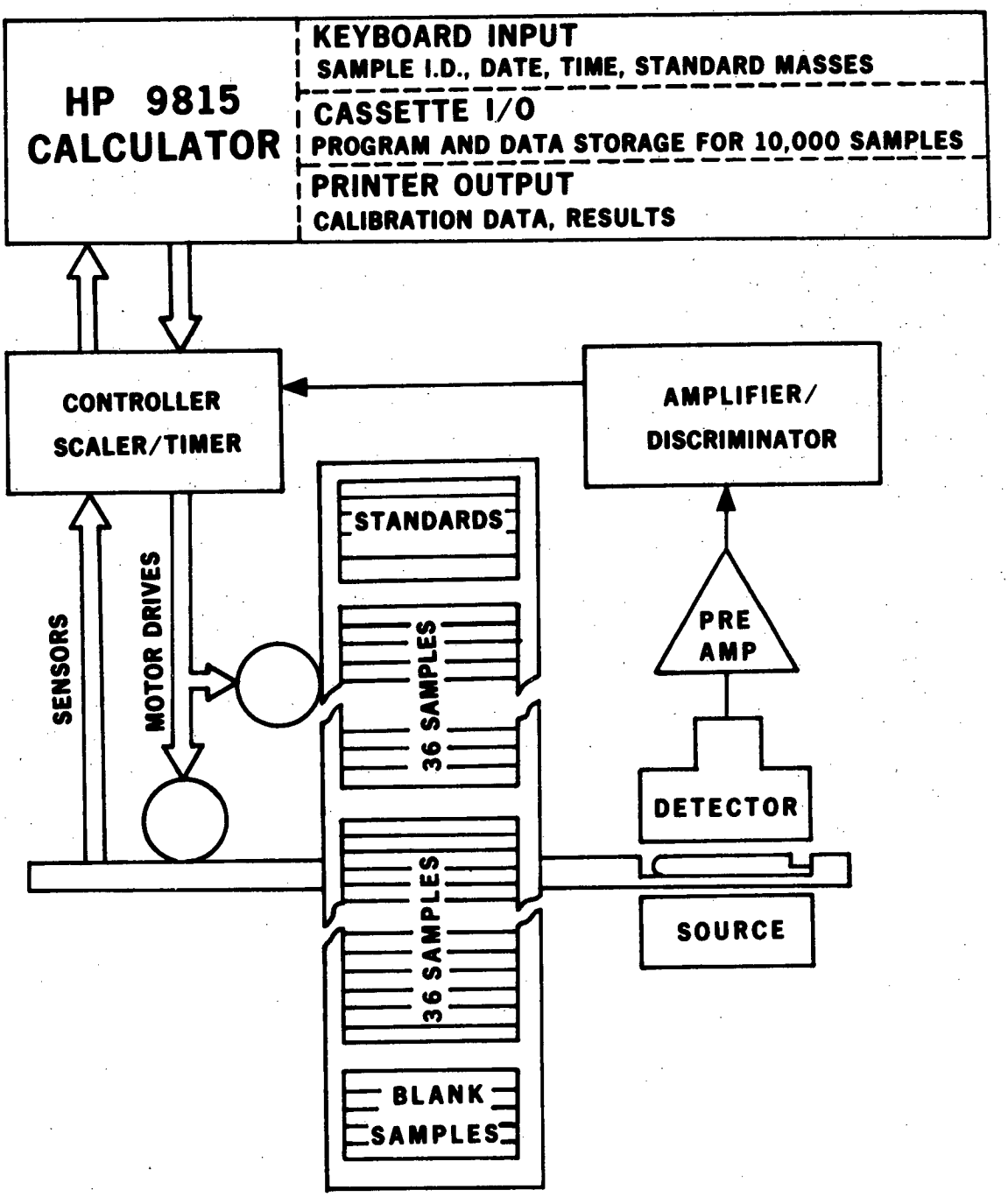


Figure 5. Automatic sample handling and data acquisition system used in conjunction with the beta-gauge.

The control of the system is incorporated into a Hewlett-Packard 9815 Calculator. An interface module is used to execute the instructions from the calculator. The unit also includes a scaler and clock which are used to count the pulses from the discriminator and communicate the result to the calculator.

Additional analysis data such as sample numbers, calibration masses, date and time are entered via the calculator keyboard. This information is used to control the analysis procedure, calculate the calibration curve, and file the results in the proper location. The cassette facility included with the calculator is capable of storing the necessary program files and the data for 10,000 samples in each cassette. Since the tare weight must be individually stored and subsequently matched to the final weight for each slide, the large storage capability allows one considerable flexibility in the handling of samples. For a typical study which might require less than 10,000 total samples, the programs would accommodate the analysis of these samples in more or less random order. Final output of the data can be either performed by the printer or the calculator or it can be transferred from the calculator to a larger facility using a standard interface.

In the normal sample running procedure, an entire sequence of standards and samples is run for a given counting period and the counts stored in a buffer. Following completion of the entire stack, the stored standard masses are fitted to the observed data using a least squares method and the results printed. The deviations of the calculated masses from the stored masses are also printed for both the thin film standards and the filter blanks. Additional statistical tests can then be printed as an indicator of system performance. The masses of the samples are then calculated and stored either as tare weights, or as tare weight together with the added mass in the case of exposed filters.

SECTION 4

PRECISION AND ACCURACY

The precision of the beta-gauge instrument can be defined as the reproducibility with which a given value can be obtained from the measurement of an unknown mass. It will include the effects of counting statistics and electronic stability on both the measurement of the calibration standards and the unknown samples. It can also be affected by possible variations in absorption characteristics as a result of misalignment of the standards and unknowns in the instrument.

The accuracy of the measurements is defined in terms of the comparison of the beta-gauge results with totally independent but equivalent methods of measurement. In the case of a single mass measurement of a given sample, the accuracy of the results depend upon the quality of the standards and validity of the calibration procedure together with any artifacts which might affect the application of a given calibration curve to the assignment of unknown masses. Included in the category of artifacts would be particle size effects, filter substrate inhomogeneity and possible atomic number dependence of the mass absorption coefficient.

In the case of a difference measurement such as employed when determining the deposited mass on a substrate, the question of precision and accuracy must be carefully interpreted. If we can associate a root mean square variation with both precision and accuracy (σ_P and σ_A, respectively), then the total uncertainty in the measurement is obtained by combining these results in normal quadrature addition. Two different cases are possible. If we perform both the tare weight and final weight measurement on the same instrument using the same calibration standards and assuming negligible particle size or filter homogenity effects, then the contribution to the combined error due to the calibration uncertainty is correlated between the two measurements and the error is:

$$\sigma^2 = 2\,\sigma_P^2 + \sigma_A^2 \qquad (4)$$

If the two measurements are performed on different systems or using completely different calibration procedures, then the errors are uncorrelated and the combined uncertainty is:

$$\sigma^2 = 2\,\sigma_P^2 + 2\,\sigma_A^2 \qquad (5)$$

Since the uncertainty in the calibration factors is typically a few percent compared to a precision of a fraction of a percent, the effect of Equation 5 is to increase the error in the case of independent tare and final weight measurements.

A far worse condition can exist if there is a systematic bias of the calibration curve employed in one beta-gauge measurement relative to the other. If we wish to detect a deposit of 10 $\mu gm/cm^2$ on a 1 mg/cm^2 substrate, a shift of 1% in calibration slope between the two weighings can completely eliminate any observed deposit. Since it is extremely difficult to maintain accuracies below this level, such errors can easily occur. For these reasons, it is important that the beta-gauge system be maintained in as stable a configuration as possible so that measurement before and after exposure can be performed under identical conditions. In cases where unavoidable modifications in detector-source geometry occur, repeated measurement of standard samples should be used to determine if any systematic calibration shifts have occurred.

PRECISION

The precision of the beta-gauge measurement depends both on statistical fluctuations associated with normal counting experiments and on uncontrolled, random fluctuations in counting rate or sample position. Ideally the contributions due to the latter effects can be minimized with the result that the precision is determined principally by counting rate and analysis time.

Beginning with Equation 3 we can derive an expression for the error associated with the calculated mass as follows:

$$\sigma^2(x) = \left(\frac{\partial x}{\partial \mu}\right)^2 \sigma^2(\mu) + \left(\frac{\partial x}{\partial \ln I_0}\right)^2 \sigma^2(\ln I_0) + \left(\frac{\partial x}{\partial \mu}\right)\left(\frac{\partial x}{\partial \ln I_0}\right) \text{Covar}(\mu, \ln I_0) + \left(\frac{\partial x}{\partial I}\right)^2 \sigma^2(I) \qquad (6)$$

$$\sigma^2(x) = \frac{(\ln I_0 - \ln I)^2}{\mu^4} \sigma^2(\mu) + \frac{1}{\mu^2} \sigma^2(\ln I_0) - \frac{(\ln I_0 - \ln I)}{\mu^3} \text{Covar}(\mu, \ln I_0) + \frac{1}{\mu^2 I^2} \sigma^2(I) \qquad (7)$$

The first three terms in Equation 7 are associated with the errors incurred in the linear least squares fitting procedure. The Covar $(\mu, \ln I_0)$ term is the usual error term arising from the interdependence of the slope and intercept when fitting a straight line to the lnI vs. x calibration

curve. The final term in the equation represents the statistical variation associated with the counting measurement on the unknown mass.

The dependence of the error on terms involving inverse powers of μ indicates the importance of choosing a source which experiences maximum attenuation. It can also be shown that the errors obtained from the least squares fitting procedure are proportional to the relative errors associated with the measurement of the individual I values. If we can assume that the standards and unknowns are measured at approximately the same counting rate and for the same interval, then

$$\sigma^2(x) \;\alpha\; \frac{\sigma^2(I)}{I^2} = \frac{1}{It} \qquad (8)$$

This gives the expected result that the total precision of the measurement scales as $t^{-1/2}$ where t is the counting interval.

Table 2 gives a summary of results testing the precision of the current beta-gauge design. These represent repeated measurements on a series of ten filters using the same calibration standards for each measurement. The nominal counting rate was 1.2×10^5 sec^{-1} and a 100 second interval was used. If we calculate the root mean square deviation under these conditions assuming statistical fluctuations only, we obtain a value of $\pm$ 2.56 $\mu g/cm^2$. This is consistent with the experimentally measured value. The temperature range is included in the table since it is known to be the external parameter which will most seriously affect the system stability presumably through variations in detector capacitance, amplifier gain and stability.

ACCURACY

Primary gravimetric mass standards in the form of thin, uniform films can normally be prepared to an accuracy of $\pm$ 1 $\mu g/cm^2$ using conventional microbalance methods. These are usually hydrocarbon films (polycarbonate, for example) which are weighed and mounted in standard sample holders. Mass values range from 600 to 6000 $\mu g/cm^2$ depending upon the average filter mass to be measured. A series of measurements of lnI vs. mass are then fitted to a straight line and the average value of μ and I_0 are computed. The value of the standard masses are then adjusted slightly to conform to the straight line fit. These adjustments compensate for small variations in the measured mass due to possible non-uniformities in the thin films and any non-linearities in the mass absorption curve in the vicinity of the least squares fit. Following these adjustments, subsequent fits to the standard typically exhibit root mean square deviations of $\pm$ 3 $\mu g/cm^2$.

Of more serious concern to measurement accuracy are possible systematic biases which arise from the application of the thin-film calibration curve to aerosol particles collected on non-uniform filter media. Effects which must be considered include particle size, filter inhomogenity, and atomic number dependence.

TABLE 2 STABILITY TESTS FOR ROOM TEMPERATURE BETA-GAUGE. MEASUREMENTS REPRESENT PRECISION IN THE CALIBRATION PARAMETERS AND CALCULATED MASSES WHICH WERE OBSERVED IN THE REPEATED MEASUREMENT OF NINE THIN-FILM STANDARDS.

Parameter	Average Deviation
I_o (blank counts)	12145622 ± 19540
ln I_o (fitted intercept)	14.0794 ± 0.0018
μ (fitted slope)	$1.5468 \times 10^{-4} \pm 2.9 \times 10^{-7}$ $cm^2/\mu g$
Mass ($\mu g/cm^2$)	686.1 ± 2.9
	1093.8 ± 2.3
	697.8 ± 2.2
	729.1 ± 1.9
	773.5 ± 1.8
	341.4 ± 2.0
	301.8 ± 2.7
	357.9 ± 3.3
	302.1 ± 2.6
Average deviation	± 2.5 $\mu g/cm^2$
Temperature range	24.6° ± 1.7° C

PARTICLE SIZE AND FILTER INHOMOGENEITY

Particle size and filter inhomogenity effects are closely related. Both arise because the measured mass per unit area represents the average over a non-uniform mass distribution arising either from a finite number of discrete particles or from a variable thickness substrate. In gravimetric mass determinations, these non-uniformities present no problem since the average mass per unit area can be computed directly from the total mass and area. However, in the beta-gauge measurement, the mass is related to the measured quantity via an exponential function. Insofar as the averaging is no longer performed linearly, possible errors can be introduced.

A simple method for estimating the effect assumes that the particles are in the form of cubes lying on a uniform substrate. Assuming N cubes per square centimeter with linear dimensions d and density ρ, then the mass per unit area which one would measure by direct gravimetric means would be:

$$x\ (g/cm^2) = Nd^3\rho + t \tag{9}$$

where t is the substrate thickness (the use of cubes instead of other particle shapes is done to simplify the calculations. In general, more complicated shapes result in a smaller particle size effect than is experienced by cubes). If the measurements are performed using a beta-gauge with characteristic calibration constants of μ and I_0, then the mass must be derived from the following attenuation data.

$$I = I_0 \left\{(1-Nd^2) + Nd^2 e^{-\mu d}\right\} e^{-\mu t} \tag{10}$$

This equation describes a model in which beta particles incident on a fraction of the filter area (Nd^2) undergo an attenuation $e^{-\mu t}\ e^{-\mu d}$. The remainder of the beam undergoes an attenuation $e^{-\mu t}$. The application of the standard thin-film calibration curve requires that the mass x' be obtained by interpreting the observed intensity I in Equation 10 according to Equation 3.

The ratio of x'/x is a measure of the error introduced as a result of finite particle size. Figure 6 is a plot of this ratio as a function of d for the case of ^{14}C and ^{147}Pm sources assuming a 100 $\mu g/cm^2$ deposit of unit density particles. In the small particle range, the number density of particles approaches that of a thin film and the discrepancy vanishes. For very-large particles, one can see that in the limit of a few very-large cubes, the attenuation is proportional to the area of the particle compared to the total filter. The mass of the particle is then practically undetected. The higher attenuation experienced by the ^{14}C source causes it to be more susceptible to particle size effect according to the model. If we allow ourselves to interpret the linear dimension d in terms of aerosol particle size, then we see that below 15 μm particle diameter, the discrepancy will be less than 5% for a ^{147}Pm beta-gauge source. Although the model used is relatively simple, it is useful in that it gives an upper limit to the observed effect. In the data processing normally employed, no correction for particle size effects are made.

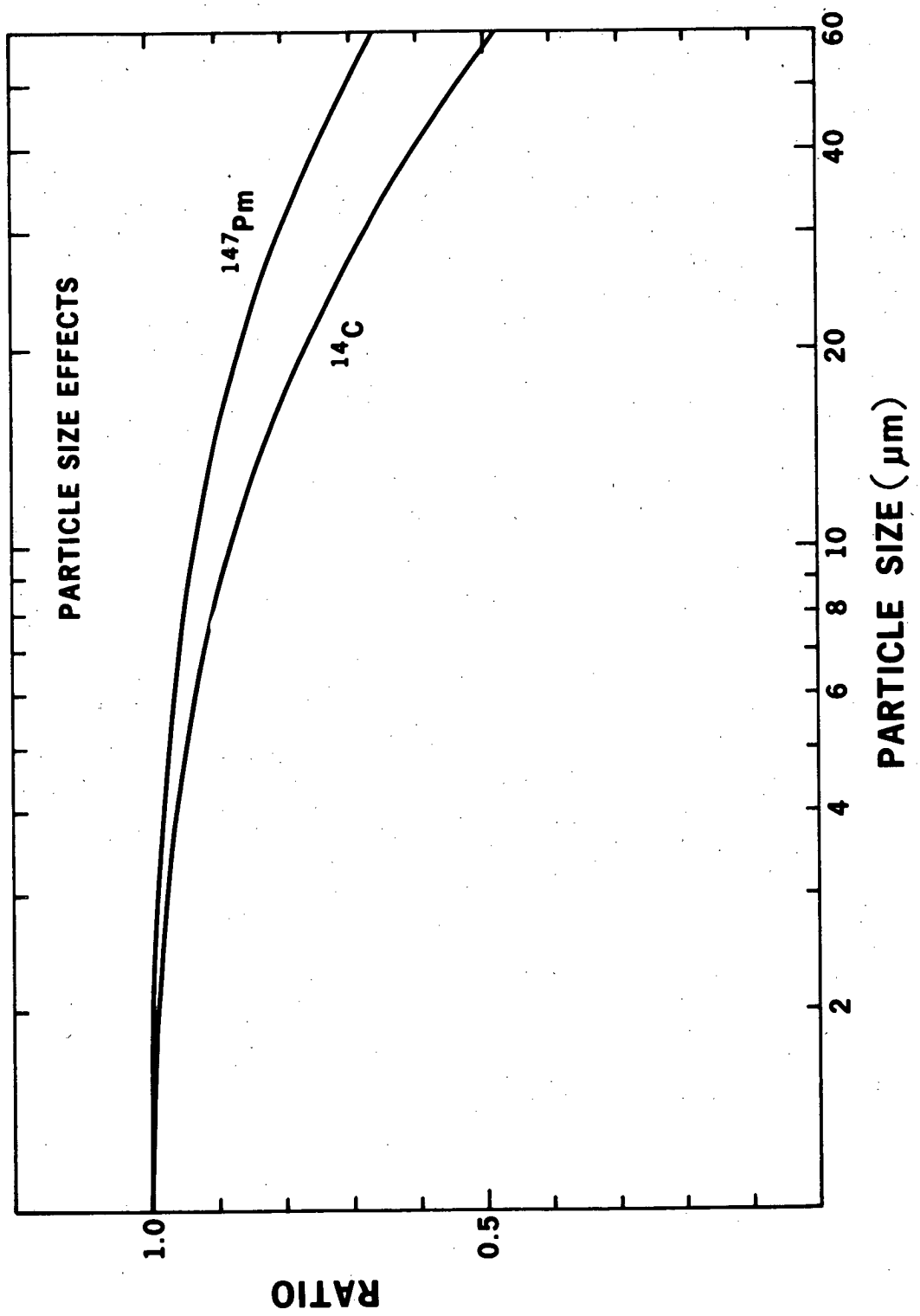


Figure 6. The discrepancy in beta-gauge mass measurements as a function of particle size for the case of two commonly used isotopes.

Inaccuracies due to filter inhomogeneities can be estimated using a similar calculation. We assume that the small-scale inhomogenities in the filter can be approximated by a model in which the filter thickness varies by a factor of two. If we furthermore assume that the total area of the thicker portion is one-half the total area, then calculations similar to Equation 10 can be performed to estimate the discrepancies which arise from the application of the uniform thin film calibration curve. The result is expressed in Equation 11.

$$x'/x = \frac{2}{3d\mu} \left\{ \ln(e^{-\mu d} + e^{-2\mu d}) - \ln 2 \right\} \qquad (11)$$

where d is the thickness of one-half the filter area and 2d is the thickness of the remainder. Note that in this model it does not matter whether the inhomogeneities are small-scale or large-scale as long as the area of each portion is one-half the total. If we assume a 1 mg/cm^2 average thickness, then the discrepancies would be 0.976 and 0.987 for ^{14}C and ^{147}Pm respectively. For a 5 mg/cm^2 substrate, the corresponding numbers are 0.891 and 0.939. Although the errors are small in a relative sense, the magnitude of the absolute error ranges from 13 μg/cm^2 to 109 μg/cm^2 in the least favorable case. The discrepancy vanishes when the difference between initial and final masses are calculated, although, once again, the importance of using identical systems for both mass measurements is emphasized. Discrepancies are minimized for the case of thinner substrates and higher energy beta-particles.

The presence of large-scale inhomogeneities in the filter substrate coupled with a slight non-uniformity in the spacial distribution of the radioactivity emitted from the source can produce similar discrepencies. These can be observed either when non-identical beta-gauge measurement are performed or, in a much more likely case, if the filter is not placed in a reproduciable geometry in the instrument. This applies both to rotations and translations of the sample relative to the axis of the source-detector system. Again the effect can be eliminated by the use of identical measurement produces for both tare weight and final weight determinations.

ATOMIC NUMBER DEPENDENCE

The process by which the beta-particles interact within the sample depends upon the number of electrons in the sample which scatter the incident beam. The validity of the beta-gauge method depends upon the proportionality between the number of electrons in the sample and the total mass and also upon the equivalence of all electrons in terms of their scattering properties. The fact that the range of electrons expressed in mg/cm^2 depends somewhat upon the atomic number of the absorber (see Figure 3), indicates that some departure from this simple behavior is expected.

We have performed measurements of the mass absorption coefficient as a function of atomic number for several substrates. The procedures were the same as employed in normal calibration runs except different thin film materials were used. Table 3 is a summary of the results. The measured mass absorption coefficients are also presented graphically in Figure 7 as a function of Z/A.

TABLE 3 MEASURED MASS ABSORPTION COEFFICIENTS FOR SUBSTANCES WITH VARYING EFFECTIVE ATOMIC NUMBER AND MASS.

MATERIAL	ATOMIC NUMBER/ ATOMIC MASS Z/A	MASS ABSORPTION COEFFICIENT (cm^2/g)
Gold	0.401	0.217
Beryllium	0.444	0.116
Copper	0.456	0.173
Nickel	0.477	0.178
Aluminum	0.482	0.156
Polyvinyl dichloride	0.495	0.165
Polyimide	0.517	0.141
Polycarbonate	0.537	0.154
Polyethylene	0.570	0.167
Polypropylene	0.570	0.165

From the plot shown in Figure 7, it is apparent that no simple relationship between μ and Z/A can be easily derived. For pure elemental samples we have $Z/A < 0.5$ and the data seem to follow a straight line dependence. The values for hydrocarbon films vary only slightly for Z/A values $0.48 < Z/A < 0.57$. A smooth curve can be drawn through the experimental points with the exception of the measurement for Be. Be represents a somewhat unique case in that it is an elemental sample with $Z/A = 0.44$, but is also the lightest element standard with $Z = 4$.

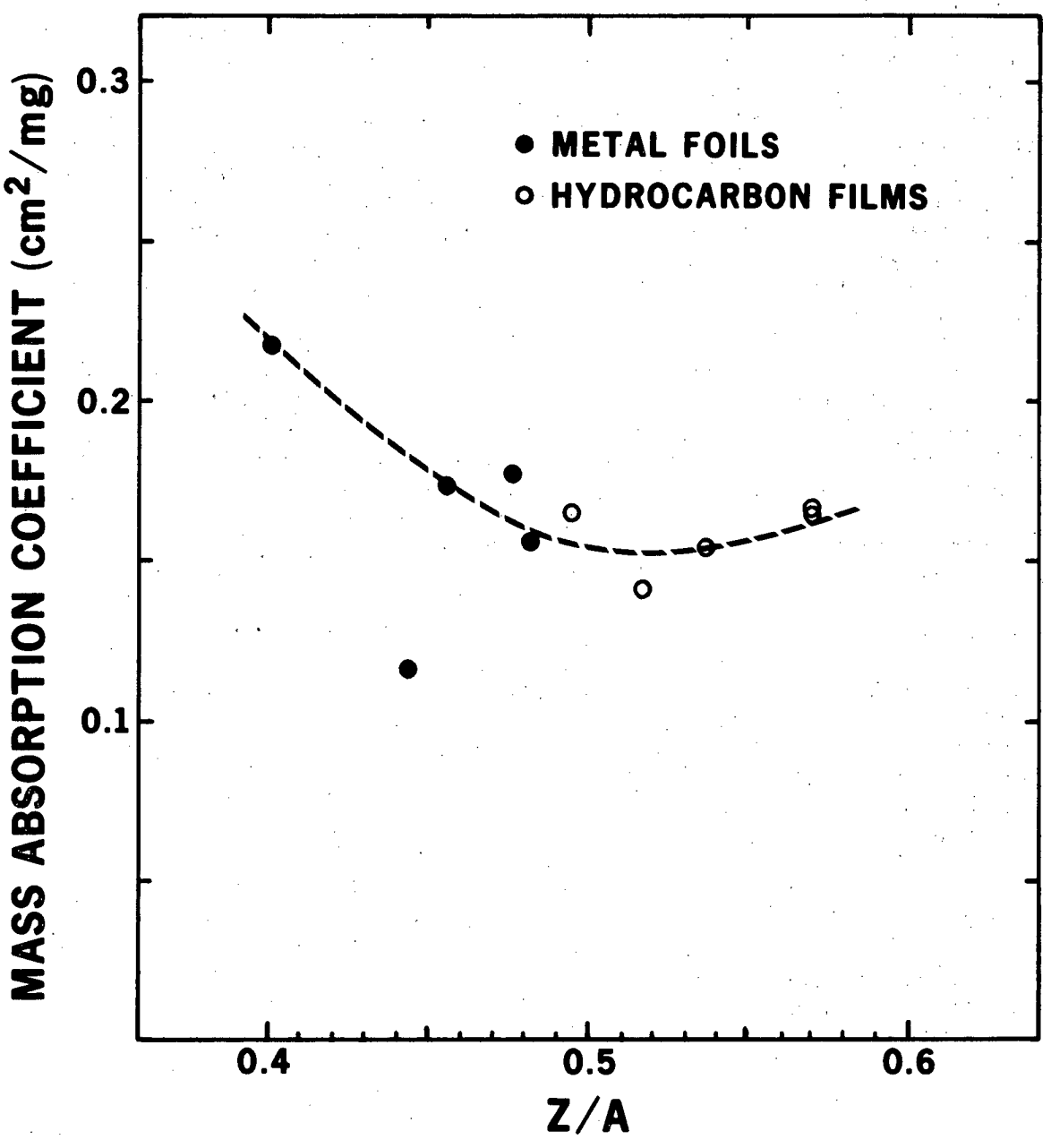


Figure 7. Measured values for the mass absorption coefficients as a function of atomic number and atomic mass.

The atomic number dependence of the absorption coefficient can be partially understood by considering in greater detail the energy loss processes for electrons. As evident in Figure 2, the total range of electrons expressed in mg/cm^2 increases as a function of atomic number. This would imply a lower mass absorption coefficient for the heavier elements which is opposite to the behavior observed. However, as noted earlier, in addition to the discrete energy loss processes which occur during collisions, there is also a change in the direction of the scattered particle. This average angular deflection is a function of atomic number and increases for the heavier elements. A typical trajectory for an electron in Be is relatively straight compared to the case of Au where a sizeable fraction of the electrons can actually be backscattered from the foil.[11] It is this strong angular dependence and its relationship to atomic number which results in the observed behavior of mass absorption coefficient with Z/A. The anomalously low absorption coefficient for Be can also be explained by this simple interpretation.

Although a detailed model for the Z/A dependence cannot be easily calculated, the effect of such variations upon realistic aerosols can be estimated. If we neglect the anomaly of Be and assume a dependence described by the curve shown in Figure 7, then the errors resulting from applying a hydrocarbon thin-film calibration to variable Z particles can be estimated. Table 4 gives the percent error in the mass measurement for various commonly encountered aerosol compounds when the mass measurement is interpreted in terms of the the normal calibration procedure.

As can be seen from the data, significant problems do not occur until one reaches the Pb compounds where errors of 30% can be expected. However, insofar as typical urban aerosol composition normally contains much less than 10% of such Pb compounds, the error introduced in the total mass measurement is minimal. In special cases where large Pb or other heavy element concentrations are observed, it should be possible to apply a correction to the calibration produced to reduce any discrepancy due to atomic number dependence.

The fact that there is some variation in μ with Z/A again emphasizes the importance of maintaining a stable configuration in the beta-gauge calibration and measurement system. A slight variation in effective atomic number brought about by using different standards or changes in the material used for detection windows, absorbers, etc., can cause apparent shifts in the measured masses.

TABLE 4 EFFECT OF ATOMIC NUMBER DEPENDENCE ON THE MEASURED MASS OF SEVERAL COMPOUNDS. COLUMN FOUR GIVES THE DISCREPANCY WITH RESPECT TO THE POLYCARBONATE STANDARDS.

Compound	Z/A	μ (cm^2/mg)	Ratio to Standard
$(NH_4)_2SO_4$	0.530	0.153	0.99
$NH_4H\ SO_4$	0.521	0.152	0.99
$CaSO_4 \cdot H_2O$	0.511	0.152	0.99
SiO_2	0.499	0.154	1.00
$CaCO_3$	0.500	0.154	1.00
Carbon	0.500	0.154	1.00
Fe_2O_3	0.476	0.163	1.06
NaCl	0.478	0.172	1.12
$PbSO_4$	0.429	0.193	1.25
$PbCl_2$	0.417	0.204	1.32
PbBrCl	0.415	0.206	1.34
Calibration value	0.154		

SECTION 5

RESULTS AND SUMMARY

The ultimate test of the beta-gauge method for aerosol mass measurement consists in comparison of results with those obtained by more conventional methods. The commonly accepted method for mass measurement is gravimetric measurement using microbalance techniques. The results from several independent studies which involved intercomparison of beta-gauge and gravimetric mass determinations are now available. Data have been selected from these studies in which the beta-gauge instrumentation was equivalent to the system described in this paper.

Figure 8 shows scatter plots of data obtained in a side by side sampling intercomparison performed in Charleston, W. Virginia in May, 1977.[12] The data quoted herein and the description of the sampling and analysis protocol are taken from Reference 12. The mass concentrations are quoted in terms of $\mu g/m^3$ referred to the original atmospheric aerosol. Figure 8A compares the results of Rodes obtained using a high-volume sampler and gravimetric weighing with those from a dichotomous sampler and beta-gauge mass determinations. The results for the latter case were calculated as the sum of the coarse and fine fractions. The average slope of the data in the scatter plots was calculated to be 1.23. The higher average mass obtained with the high volume sampler probably reflects the larger effective particle size cutoff obtained with this sampler relative to the dichotomous samples.

The plot of Figure 8B shows the results obtained from a gravimetric analysis of samples acquired with separate dichotomous samplers relative to the earlier beta-gauge results. The gravimetric measurements are those quoted by Dzubay in Reference 12. The data shown are for the fine particle fractions only since the upper cutoff for each of the dichotomous samplers was unknown. The excellent agreement between the two data sets reflects the relative precision of the two sampling methods. The calculated slope of the line shown is 0.954.

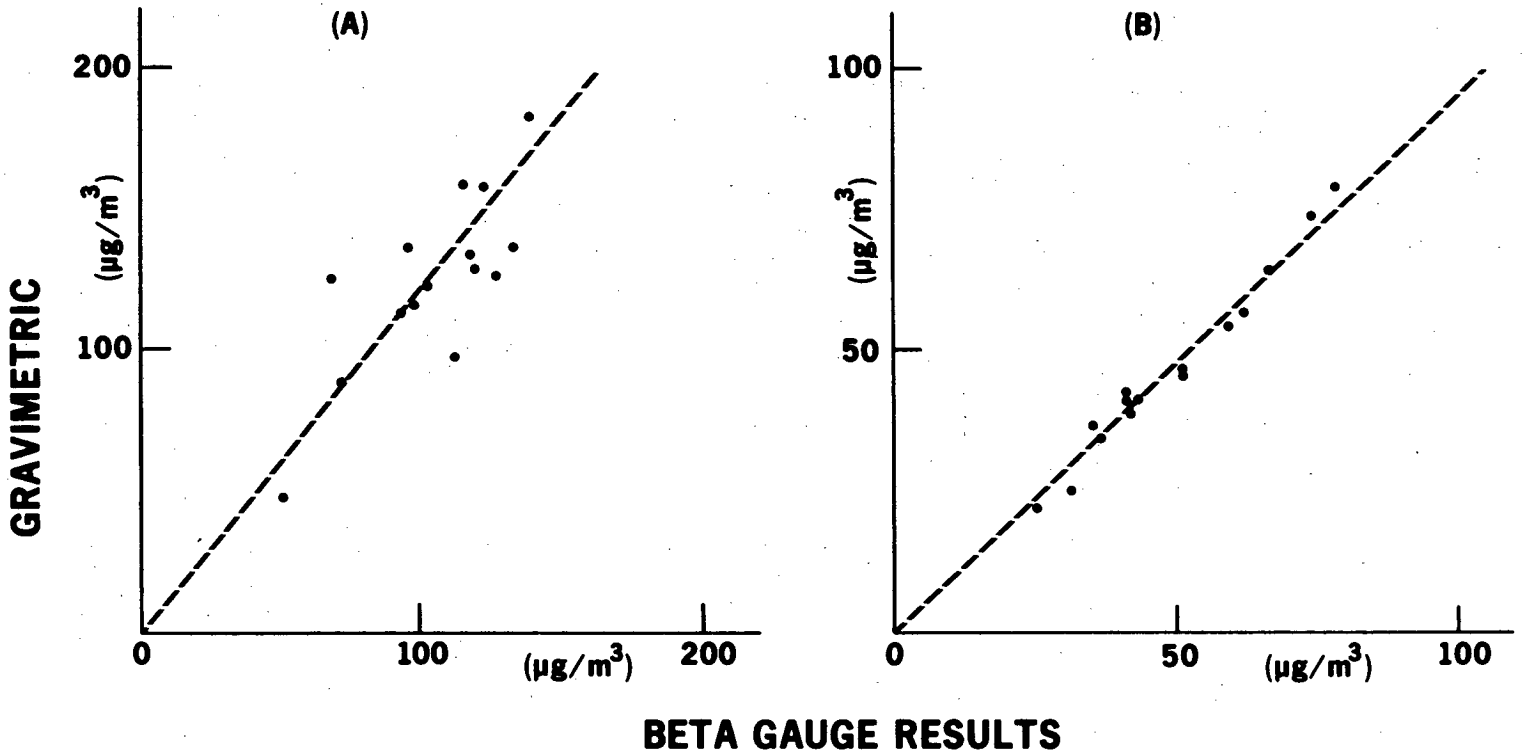


Figure 8. Comparison of beta-gauge results with those obtained by gravimetric methods. These data were obtained by comparing side-by-side samples of the same atmospheric aerosol collected by different samplers. Case A represents high volume samples vs. dichotomous. Case B was obtained with manual dichotomous vs. automatic dichotomous samplers.

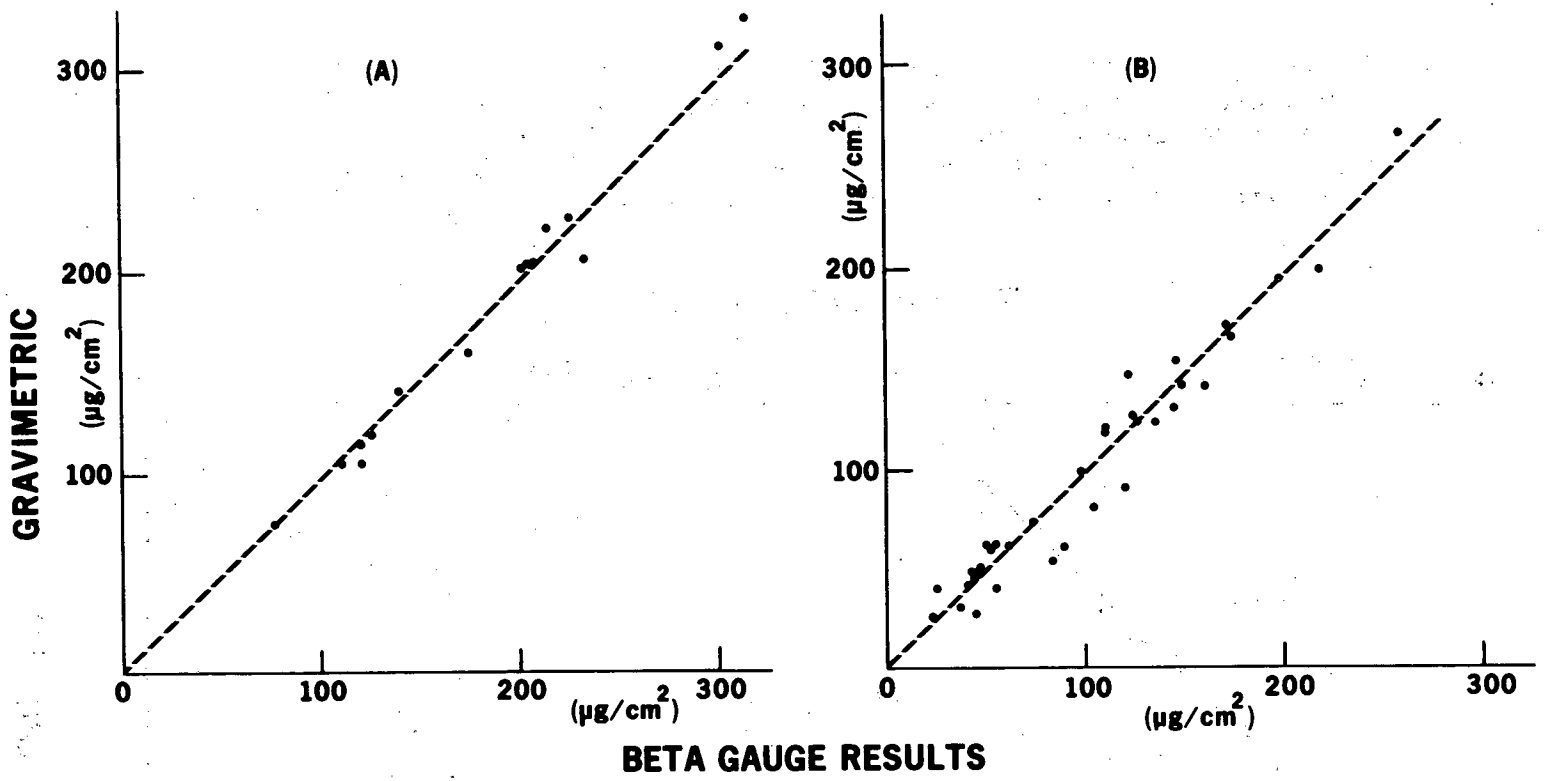


Figure 9. Comparison of beta-gauge results with those obtained by gravimetric methods. Thse data represent duplicate mass measurements on the same sample. Samples for curve A were obtained in our laboratory. The data shown in curve B were obtained from workers at EPA[13].

A more direct comparison which eliminates uncertainties due to non-equivalent sampling methods can be obtained by sampling with membrane filters mounted on thin frames which can be removed from the normal 5.1 cm x 5.1 cm carrying frame. The same sample can then be analyzed by both beta-gauge and direct weighing. Figure 9 shows the results of two such independent studies. The plot of Figure 9A was generated from data obtained in our laboratory using aerosol samples collected locally. The fine and coarse particle fractions were analyzed separately and are included in the plot a separate points. The data are quoted directly in terms of $\mu g/cm^2$ as deposited on the thin Teflon membrane filter. The observed slope of the data was calculated to be 0.973. There were some slight systematic differences observed between the coarse and fine particle fraction which are not obvious in the combined data set. This is probably due to non-uniformity of the particle deposition together with possible particle size effect as discussed earlier.

Figure 9B shows the results of a study performed at the EPA Environmental Sciences Research Laboratory.[13] Fine particle samples were acquired from an indoor aerosol and subjected to the same analysis as discussed above. Again the agreement was excellent with a calculated slope of 0.963.

SUMMARY

The beta-gauge method for the determination of the mass of atmosphere aerosol samples has been demonstrated to be equivalent in accuracy to gravimetric methods when proper attention is paid to instrumental design and calibration procedures. The advantages of automation and reduced sample handling would make beta attenuation the method of choice for larger sized monitoring programs. The present instrument design has been implemented with the capability for the automatic storage and retrieval of large data sets consistent with the large-scale approach to mass measurement.

REFERENCES

1. R. D. Evans, The Atomic Nucleus, McGraw-Hill, New York, 1955.

2. G. I. Gleason, J. D. Taylor and P. L. Tabern, "Absolute Beta Counting at Defined Geometries", Nucleonics 8 (1951) 12.

3. "Symposium on Applied Radiation and Radioisotope Test Methods", ASTM Special Technical Publication No. 268, (1959).

4. C. E. Compton, "The Versatility of Radiation Applications Involving Penetration or Reflection", Proc. Intern. Conf. Peaceful Uses of Atomic Energy, Genoa (1955) 15, 124.

5. P. Lilienfeld, "Beta-Absorption-Impactor Aerosol Mass Monitor", Am. Ind. Hygiene. Assoc. J. 31 (1970) 722.

6. P. Lilienfeld, "Design and Operation of Dust Measuring Instrumentation Based on the Beta-Radiation Method". Staub-Reinhalt Luft 35 (1975) 458.

7. E. S. Macias and R. B. Husar, "High Resolution On-Line Aerosol Mass Measurement by the Beta Attenuation Technique". Proceedings of the Second International Conference on Nuclear Methods in Environmental Research. Edited by J. R. Vogt and W. Meyer. CONF-740701, p. 413 (1970).

8. M. J. Berger and S. M. Seltzer, "Tables of Energy Losses and Ranges of Electrons and Positrons", in Studies in Penetration of Charged Particles in Matter, Nat. Acad. Sci. NRC Publ. 1133, (1964) 205.

9. D. W. Cooper, "Statistical Errors in Beta Absorption Measurements of Particulate Mass Concentration", Journal Air Poll. Conf. Assoc. 25 (1975) 1154.

10. B. W. Loo, J. M. Jaklevic and F. S. Goulding, "Dichotomous Virtual Impactors for Large-Scale Monitoring of Airborne Particulate Matter", in Fine Particles: Aerosol Generation, Measurement, Sampling and Analysis, B. Y. H. Liu Ed. (New York, Academic Press, 1976). 311.

11. G. D. Archard, "Back Scattering of Electrons", Jour. of App. Phys. 32 (1961) 1505.

12. D. C. Camp, A. L.VanLehn and B. W. Loo, "Intercomparison of Samples Used in the Determination of Aerosol Composition", Interagency Energy-Environment Research and Development Series, Report No. EPA-600/7-78-118.

13. W. J. Courtney, Northrup Services, Inc., Research Triangle Park, NC, private communication.

U.S.GPO:1980-698-169/F-122

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720