

A Spiked, Mixed-Radionuclide, Mock "Soil"
Marinelli-Beaker Calibration Standard
For γ -Ray Spectrometry

A Project Report Prepared

for the

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by

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A spiked, mixed-radionuclide, mock "soil" calibration standard (in a 1-L Marinelli beaker configuration) was gravimetrically prepared, and calibrated by high-resolution γ -ray spectrometry. The matrix consisted of a well-characterized (in terms of densities, particle sizes, etc.) and blended standard Ottawa sand. The matrix was spiked with ^{241}Am , ^{109}Cd , ^{57}Co , ^{139}Ce , ^{203}Hg , ^{113}Sn , ^{85}Sr , ^{137}Cs , ^{88}Y , and ^{60}Co . Source homogeneity and possible spike losses were evaluated for every spiking radionuclide. Measurements on aliquants (30 g samples out of 1850 g of spiked matrix) taken as a function of blending times (40 min to 400 min) indicated source homogeneity to within several percent. The only observed spike loss was for ^{203}Hg which is due to the chemical instability and volatility of deposited mercury compounds. A quantitative, verifiable, and efficacious spiking protocol was devised and developed as part of this work, and used to prepare the Marinelli-beaker calibration standard.

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Project objectives and overview

The objectives of this project were: (i) to prepare and calibrate a spiked, mixed-radionuclide, mock "soil" source (in a 1-L Marinelli beaker configuration) that can be used as a transfer calibration standard for γ -ray spectrometry; and (ii) to devise and develop a spiking and preparation scheme that is easily reproducible (using readily available stock materials), quantitatively reliable (in terms of being able to relate γ -ray emission rate concentrations for the spiking solutions to the emission rates for the mock "soil" in the Marinelli Beaker), and verifiable (in terms of source homogeneity, accounting for possible losses of spiking radionuclides, etc.).

Two mock "soil" standard source approaches were initially pursued. They were:

1. a standard Ottawa sand (designated OS); and
2. a granular sodium chloride (designated GS).

One Marinelli beaker source of each (along with matched blanks) have been prepared. Evaluations (such as for source losses, source homogeneity, etc.) and final high-resolution photon-emission calibrations on OS have been completed. Although GS was also prepared and underwent a number of preliminary investigations, it was not thoroughly calibrated since the original choice of OS was found to be adequate. The source OS could be fully calibrated at a later time if there is some perceived need or use for this type of source matrix.

Mock "soil" matrix selection considerations

The original selection of Ottawa sand for the mock "soil" matrix was initially considered to be a possibly poor to mediocre choice. Its principal advantage is that it is readily available with well-characterized physical properties. It is, obviously, granular and can be obtained (as 20-30 mesh) with a fairly narrow particle-size distribution. Particle size measurements by this laboratory have demonstrated that over 98% of the particles (by mass) are in a range 0.59 mm to 0.84 mm (see Annex A). Bulk density, grain density, and volume packing determinations were also made. How well this matrix might simulate finer mesh soils, e.g., 200 to 325 mesh (0.075 to 0.045 mm), and soils of different densities and other compositions is another matter.

Our principal initial concern in using Ottawa sand was that we thought it may have a low adsorption capability. The concern would be that the spiking radionuclides may not easily adhere to the sand particles and/or may be lost in handling (e.g., with agitation during blending) or in usage (e.g., with settling in the Marinelli beaker). Hence, the alternative granular salt matrix was also pursued, mainly because of the above concern with Ottawa sand. We reasoned that in the case of the granular salt, the spiking would not rely on physical or Van der Waals' adsorption of the spiked radionuclides on particles of silica or mixed silicates. Rather, it relies on actual chemical adsorption (chemisorption) which results in firm chemical bonds between the spiking radionuclides and matrix crystals. When the spiking solution is deposited as fine droplets onto the sodium chloride granules, some portion of the crystals dissolve; but the deposited solution immediately re-crystallizes as mixed salts of the spiking radionuclide and NaCl (since the dissolved solution is super-saturated).

In retrospect, it is now evident that Ottawa sand is sufficiently adsorptive to adequately serve as the spiked matrix. During the course of this project however, we also learned what criteria one might use to select more adsorptive matrices of either real soils or stone aggregates. These might include (a) soils containing clay minerals that show a marked adsorptive capacity; and (b) other pulverized, granular stone aggregates that are known to have greater "strength", i.e., better adsorption properties. The "strength" of a cement prepared from a given aggregate can be used as a crude guide or relative measure of the adsorptive capability of the aggregate. One might therefore expect a pulverized limestone to be worse than Ottawa sand, and certain Georgian marbles to be better, for examples.

Preparation of Marinelli-beaker calibration standard OS1

Preparation schema

The protocol used for the preparation is outlined in Figure 1. The principal features of the scheme include:

The spiking was performed with the mock "soil" matrix in a filter paper liner which allowed evaluation of any loss of spiking solution. This aspect is unique in comparison to all other published methods used for spiking in which heroic efforts are normally required to assay the spiking apparatus for any residual activity.

A spiked "hot spot" reference source contained a well known quantity of spiking master solution and allowed comparative measurements with other samples. This sample was not homogeneous however, and small differences in relative measurements naturally arose because of this.

The dried spiked matrix was diluted with additional matrix and blended in a high-efficiency vee-cone blender to assure source homogeneity.

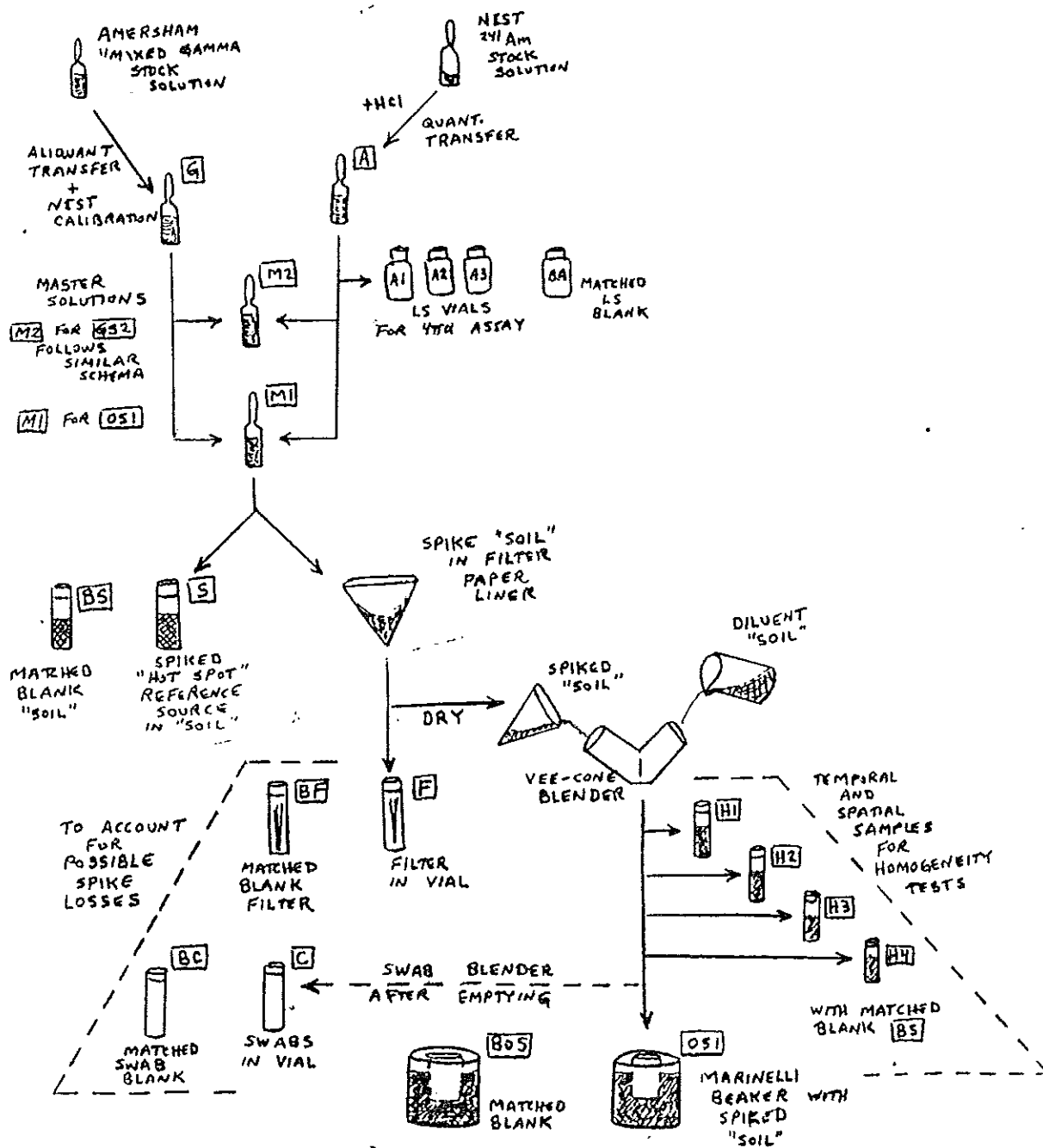
Homogeneity could be checked both with spatial aliquants of the spiked matrix and temporally as a function of blending time.

All samples had matched blank counting sources.

All transfers of solutions and matrices were gravimetrically determined (usually with independent verification).

The procedure was found to be very quantitative (both in terms of retention of the chemically-stable spiking radionuclides and recovery of the spiked matrix), verifiable (in terms of source homogeneity, accounting for possible spike losses, etc.), and very easy to replicate. Additional details on the protocol will be described in a separate publication by Collé and Schima [*A Quantitative, Verifiable, and Efficacious Protocol for Spiking Solid, Granular Matrices with Radionuclidic Solutions*, to be published].

Figure 1.
 Schema for the spiking and preparation of the mock "soil"
 Marinelli beaker calibration standard.



Marinelli beakers

The Marinelli beakers used in this work were nominal 1 liter, polyethylene, standard configuration containers with a type designation of "130-G" which were supplied by GA-MA Associates, Inc.

The beakers were found to have a total mass (when empty) of $148.17 \text{ g} \pm 0.13 \text{ g}$ where the cited uncertainty is a standard deviation with $\nu = 5$ for mass determinations on 6 beakers; and a total contained volume of $1211 \text{ cm}^3 \pm 5 \text{ cm}^3$ (at 22 C) where the cited uncertainty is a combined standard uncertainty. The latter volume measurement is based on replicate gravimetric determinations using high-purity water of known density at given temperatures for 3 beakers with 3-point extrapolations to total capped volume.

OS and GS mock "soil" matrices

The mock "soil" matrices for both standard Ottawa sand (OS) and granular sodium chloride (GS) are described and characterized in Annex A.

Stock and master spiking solutions

The master spiking solutions (labelled solutions M1 and M2 in Figure 1) that were used to prepare the Marinelli beaker sources OS and GS were prepared by combining gravimetrically-determined aliquants of stock solutions G and A in 5 mL ampoules.

Solution G was a mixed-radionuclide γ -ray reference source originally obtained from Amersham (Product code QCY.44; solution number R4-110-4; certificate M27226). The solution was in a 5-mL ampoule, and contained the usual mix of 9 radionuclides in 4 N HCl ($1.067 \text{ g}\cdot\text{mL}^{-1}$ at 20 C). The original solution was certified by Amersham for $\gamma \text{ s}^{-1}\cdot\text{g}^{-1}$ of solution for 11 photons. The contents of the original solution was gravimetrically transferred to a new NIST standard 5-mL ampoule (labelled R4-110-4a) and was re-assayed by NIST for the emission rate concentration for each of the 11 photons. The relative standard uncertainties on each emission rate concentration, as obtained from the NIST re-assay, ranged from 0.33% to 0.82%. Comparisons between the original Amersham certified values and those obtained by NIST (with decay) indicated agreement to better than 0.1% to 0.2% in general for each of the 11 photons (and was 0.5% in a worst case for the 88-keV ^{109}Cd γ ray).

Solution A was derived from a NIST ^{241}Am 2-mL ampoule (labelled LL92-241-2) which was believed to contain approximately 10.36 Bq of ^{241}Am in an unknown small volume (roughly 0.2 mL) of 1 N HCl. The activity concentration of the solution was unknown, but the total ^{241}Am activity content in the ampoule was assumed to be known based on a previous NIST assay. The contents of the original ampoule was transferred with rinsings to a new 5-mL ampoule (labelled A). The ^{241}Am activity concentration of ampoule A was assayed by $4\pi\alpha$ liquid scintillation spectrometry, and was found to be $2348 \text{ Bq}\cdot\text{g}^{-1} \pm 7 \text{ Bq}\cdot\text{g}^{-1}$ as of 1200 EST 21 September 1994. The LS assay was based on 12 replicate measurements on each of three LS samples (and matched blanks for background subtraction) that were intermittently performed over the course of 8 days. The cited uncertainty corresponds to a combined standard uncertainty.

Solution ampoules G and A, prior to their use in preparing master solutions M1 and M2, were measured in a NaI(Tl) well counter to obtain relative gross γ -ray emission rates. These rates could be subsequently compared to the results on similar measurements on M1 and M2 to independently verify

the gravimetric determinations. The relative gross rates were based on integrating the full-energy NaI(Tl) spectra from approximately 20 keV to 3400 keV which included all of the ^{241}Am to ^{88}Y photopeaks as well as sum peaks.

The gravimetrically-determined aliquants of solutions G and A in M1 and M2 were also based on "dispensed masses" obtained from differences in masses between dispensings with an aspirating pycnometer. These mass differences were also independently confirmed by the "contained masses" obtained from mass differences in the ampoules before and after dispensing. Relative differences between the dispensed and contained masses were less than 0.05% in all cases.

The gravimetric preparations of master solutions M1 and M2 could be independently verified from the constituent masses and the relative gross γ emission rates (noted above). The overall agreement between directly measured rates on solutions M1 and M2 and that obtained from the predicted weighted combinations of the rates on solutions G and A were +0.092% and 0.043%, respectively. Similar relationships between the masses and gross γ emission rates could be used to verify, for example, the mass ratio of solution M1 to M2 as well as other corresponding mass pairs. Overall, the relative emission rate verifications indicated mass agreements to typically better than 0.05%, and 0.18% in a worst case.

Calibration and evaluations of Marinelli-beaker calibration standard OS1

Standard OS1 on sealing consisted of 1715.9006 g of Ottawa sand that had been spiked with 3.938335 g of solution M1. The corresponding blank BOS contained 1725.6542 g of sand. Assuming a bulk density of $1.72 \text{ g}\cdot\text{cm}^{-3}$, the volumes of the two sources are 1.003 L and 0.998 L, respectively.

Matrix recovery

Standard OS1 was obtained by spiking approximately 230 g of sand with 4.238052 g of solution M1 which after drying was combined with diluent sand to form a total spiked Ottawa sand mass of 1846.4848 g. The total mass of Ottawa sand recovered after all operations was 1846.4619 g, which corresponds to an unaccounted-for-sand loss of 0.0229 g or a recovery of 99.999% of the total sand used. One may appreciatively note, that if one assumes a grain density of 0.00068 grams per grain, then the unaccounted-for-sand loss corresponds to about 34 grains of sand lost out of 2.72 million!

Emission rates for OS1

Based on the gravimetrically-determined spiking and dilution, and on the previously determined emission rates for solutions G and A that were used to prepare solution M1, the total emission rates for OS1 (as of the calibration reference time 1200 EST, 1 October 1994) could be calculated and are given in Table 1.

Spike losses

Other than a detected spike loss for ^{203}Hg , there was no evidence for any other radionuclidic losses in the spiking procedure. The ^{203}Hg loss is not necessarily surprising since mercury is chemically unstable when it is out of solution and dried. The spike loss for ^{203}Hg is believed to have principally occurred during the blending process and not during wetting of the sand matrix -- insofar as the

Table 1.

Gravimetrically-determined spiking of "mixed gamma" standard OS1

radionuclide	gamma-ray energy (keV)	NIST emission rate for OS1 ($\gamma \text{ s}^{-1}$) [a]	relative standard uncertainty (%)
²⁴¹ Am	59.537	1442.2	0.89
¹⁰⁹ Cd	88.0341	1126.4	0.59
⁵⁷ Co	122.0641	908.9	0.68
¹³⁹ Ce	165.857	744.1	0.45
²⁰³ Hg	279.1967	444.0 [b]	1.16
¹¹³ Sn	391.702	1774.7	0.71
⁸⁵ Sr	514.0076	1683.6	0.67
¹³⁷ Cs	661.66	5404.1	0.39
⁸⁸ Y	898.042	5201.0	0.53
⁶⁰ Co	1173.238	6989.6	0.34
⁶⁰ Co	1332.502	7014.4	0.34
⁸⁸ Y	1836.063	5436.9	0.54

[a] The emission rates are as of 1200 EST, 1 October 1994.

[b] Spiking of ²⁰³Hg was demonstrated to be nonquantitative because of its chemical instability out of solution.

spiking filter (see Figure 1) contained no detectable activities. Of course, this does not necessarily exclude the possibility that the mercury might have been lost through volatilization during the initial drying process. Such volatilization losses would not have been detected by analyses of the filter.

Table 2 illustrates the results of detected losses from three spike loss samples.

Based on low-resolution NaI(Tl) spectrometry with a well counter, initial spiking losses (for total gross γ activity) appeared to be less than 0.02%. This estimate was based on NaI(Tl) spectra analyses of spike loss samples obtained from swabbing the entire interior surface of the vee-cone blender after all the spiked OS was removed. Subsequent samples obtained from the seals and axle shafts of the blender after the blender was disassembled exhibited a total spike loss of roughly 0.36%. Firstly, this percentage could not be accounted for by losses of the OS. Its value was larger than the total unaccounted for loss of OS mass used in the spiking, blending and preparation processes. As noted above, the overall recovery of the OS mass used was 99.999% (23 mg lost out of over 1846 g). This finding suggests that at least part of the spike loss was not associated with unrecovered sand. It seems

Table 2.

Spike loss results based on NaI(Tl) gross γ measurements (over the full-energy spectra) with normalization to the "hot spot" reference spike.

sample	obtained from	fraction of M1 spike
F-OS	filter liner	< 0.00001
C2-OS	initial blender swabs	0.00012
C-OS	blender swabs after dismantling	0.0036

quite probable that the loss occurred during the blending because of detachment or volatilization of the radionuclides from the OS matrix particles. Secondly, NaI(Tl) spectral examinations of the spike loss samples strongly demonstrated that the spiking radionuclides were present in different ratios (or fractionated differently) in the loss samples than in the OS samples. It was most evident for ^{203}Hg . The location of the largest spike losses in the most inaccessible parts of the blender suggest that the radionuclides were lost as gaseous or very fine particulate matter.

This apparent preferential loss of ^{203}Hg in the spiking was confirmed by high-resolution γ -ray spectrometry on the spike loss samples, as well as inferentially from measurements on the homogeneity samples and in the beaker calibration measurements themselves (see subsequent discussions).

As indicated previously, the nonquantitative spiking of ^{203}Hg perhaps should not be surprising since such source preparation problems frequently arise out of the volatility of many mercury compounds. It has been demonstrated that the losses are such that ^{203}Hg can not be certified in the calibration of OS1. The use of any other mock "soil" matrix (such as the prepared GS2 source) may not resolve the problem since the mercury loss is likely to occur during any drying process, irrespective of the matrix used. A nearly comparable loss was found in GS2. One could of course envisage a modification of the preparation procedure by drying the spike in an atmosphere of hydrogen sulfide to precipitate HgS . But then, it is not apparent why the precipitated HgS would necessarily adsorb or adhere to the matrix grains, and would likely "shake off" the matrix during blending.

No other such radionuclide fractionation problems or losses were found for any other radionuclides in the mix.

Homogeneity

During blending, four homogeneity samples were collected at different blending times. These are given in Table 3.

Based on low-resolution NaI(Tl) spectrometry with a well counter, four homogeneity samples (collected after 40 to 400 minutes of blending) showed that the OS blend was homogeneous, both temporally and spatially, to within a few percent. This estimate was based on the total gross γ activity in the samples which was obtained from integrating the full-energy NaI(Tl) spectra. Crude analyses of the photopeaks for the individual radionuclides in the homogeneity samples demonstrated that there

Table 3.

Homogeneity samples for preparation of OS1

sample	mass of sample (g)	blending time (min)
H1-OS	33.6888	40
H2-OS	32.5688	120
H3-OS	33.3162	244
H4-OS	30.9877	400

was no substantial fractionation of the radionuclides in the samples, excepting that for ^{203}Hg . These NaI(Tl) results were, of course, at best only semi-quantitative. The relative mean gross γ activity in the 4 homogeneity samples was, however, also in agreement to within about 0.5% with that expected from the total M1 solution mass spiked in the total OS mass.

Figure 2 gives the results of these gross γ activity measurements on the samples. The "homogeneity measure" given in the figure corresponds to the mass ratio M1/OS. This was obtained by normalizing the NaI(Tl) counting rate concentrations to that obtained from a known aliquant of M1 in OS (the "hot spot" spike -- see Figure 1). The displayed results are normalized values from 4 determinations obtained by integrating the full-energy NaI(Tl) spectra. The dotted line in Figure 6 is the gravimetrically determined M1/OS ratio.

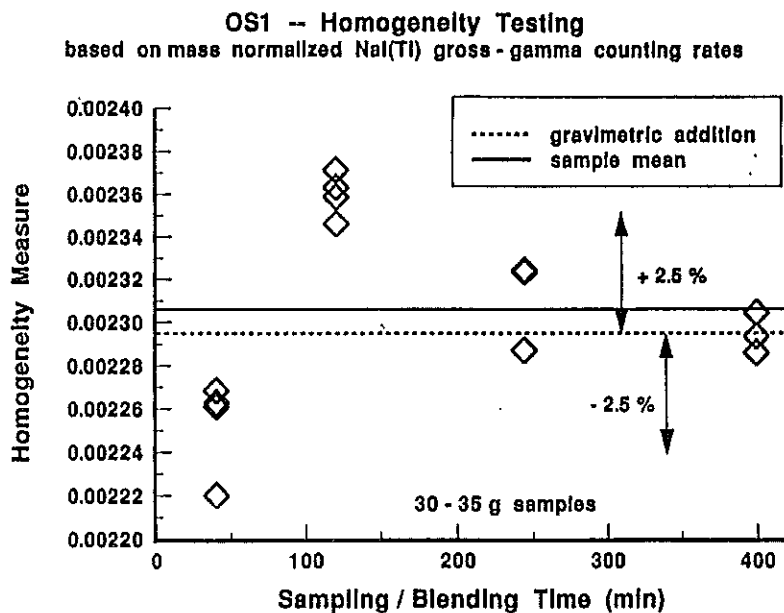


Figure 2.

High-resolution γ -ray spectrometry on the homogeneity samples of Table 3 were also performed to evaluate homogeneity for specific radionuclides. Some of the results of these measurements are given in Figure 3. These results were obtained with the NIST "X" detector (an n-type intrinsic Ge with a 1-mil Be window and having an equivalent 9.9% NaI efficiency). The results of Figure 3 are normalized to the observed emission rates obtained for sample H4 (after 400 min of blending). As shown, the emission rate for sample H1 (after 40 min of blending) is almost always invariably lower than the next three samples, suggesting that perhaps an hour or so of blending is required to achieve reasonable homogeneity. The results for ^{203}Hg are dramatic and show the progressive loss of mercury over the entire blending time. Between sample H1 and H4, the ^{203}Hg loss is nearly a factor of two -- despite that most of the ^{203}Hg was lost prior to the H1 sampling. On consideration of just the last three samples for every radionuclide, the mean relative homogeneity is typically within $\pm 2\%$ or 3% of unity (excepting that for ^{203}Hg) with relative standard deviations of comparable magnitude (see Table 4).

Table 4.

Relative homogeneity in samples H2, H3, and H4 for the individual radionuclides
as obtained with the NIST "X" detector

radionuclide	gamma-ray energy (keV)	mean relative homogeneity	standard deviation
^{241}Am	59.537	0.975	0.025
^{109}Cd	88.0341	0.983	0.021
^{57}Co	122.0641	0.993	0.007
^{139}Ce	165.857	1.027	0.028
^{203}Hg	279.1967	[1.47]	[0.43]
^{113}Sn	391.702	1.020	0.027
^{85}Sr	514.0076	0.959	0.038
^{137}Cs	661.66	0.970	0.026
88Y	898.042	1.005	0.022

Calibration

The standard OS1 was calibrated on the high-resolution NIST "T" detector which is a p-type intrinsic Ge having an equivalent efficiency of 14.5% of NaI. A summary of the calibration factors for each principal photon is given in Table 5. The calibration factors are virtually a type of apparent "efficiency" in that they are the observed counting rates from the source for each photon divided by their respective gravimetrically-determined emission rates (Table 1). The calibration factors do not include any corrections, such as source self-absorption or correlated- γ summing losses. Figure 4 illustrates these calibration factor data in terms of a conventional "efficiency curve". The obviously anomalous value for ^{203}Hg clearly demonstrates the spike loss for this radionuclide.

Figure 3.
Relative homogeneity of the individual radionuclides in four aliquants
taken as a function of blending time (40 min to 400 min)
as measured with the high-resolution NIST "X" detector.

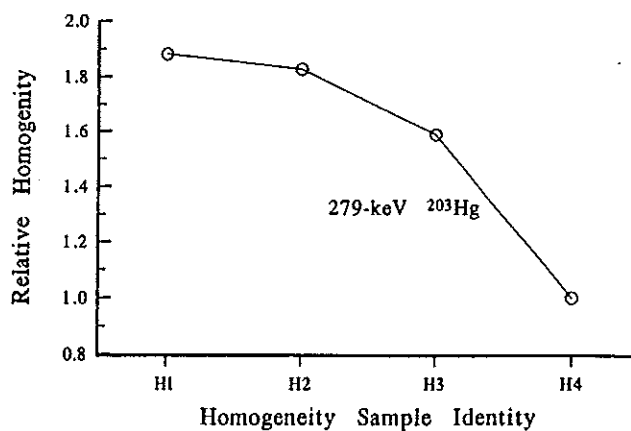
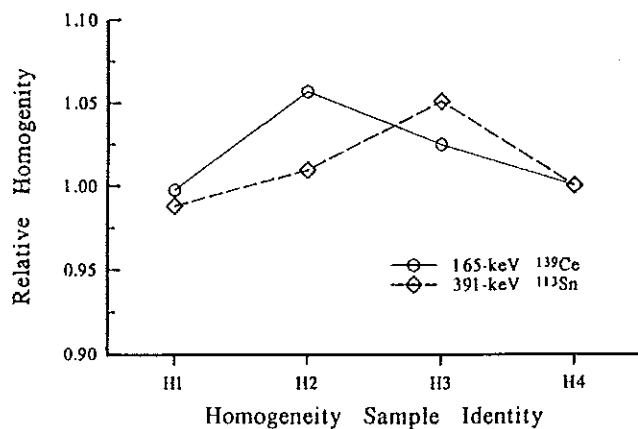
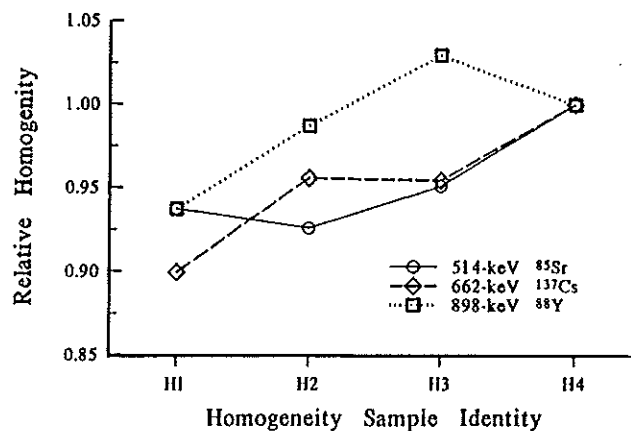
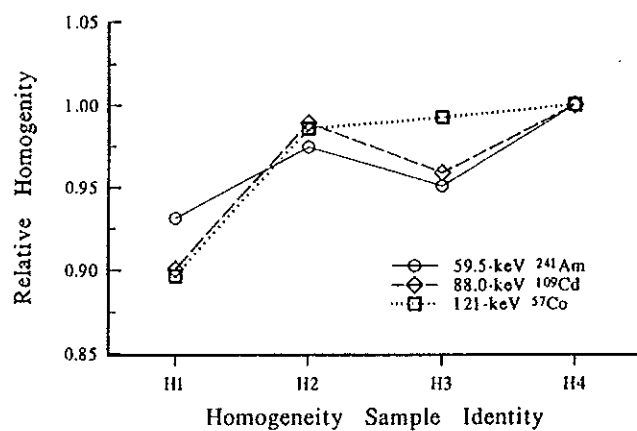


Table 5.

Calibration factors for standard OS1 as obtained with the NIST "T" detector

radionuclide	gamma-ray energy (keV)	NIST calibration factor for OS1 [a]	relative standard uncertainty (%)
²⁴¹ Am	59.537	0.005346	1.07
¹⁰⁹ Cd	88.0341	0.013905	0.69
⁵⁷ Co	122.0641	0.019576	0.74
¹³⁹ Ce	165.857	0.018256	0.58
²⁰³ Hg	279.1967	[0.00484] [b]	[1.90]
¹¹³ Sn	391.702	0.00953	0.76
⁸⁵ Sr	514.0076	0.007149	0.74
¹³⁷ Cs	661.66	0.006275	0.42
⁸⁸ Y	898.042	0.004295	0.57
⁶⁰ Co	1173.238	0.003502	0.39
⁶⁰ Co	1332.502	0.003151	0.39
⁸⁸ Y	1836.063	0.002409	0.59

[a] The calibration factor is the apparent "efficiency" given by the observed γ -ray counting rates for each photon (as of 1200 EST, 1 October 1994) divided by their respective gravimetrically-determined γ -ray emission rates for the source (see Table 1). The calibration factor does not include any corrections for source self-absorption, correlated- γ summing, etc.

[b] This value for ²⁰³Hg is not certified because of known spike losses.

Summary and Conclusions

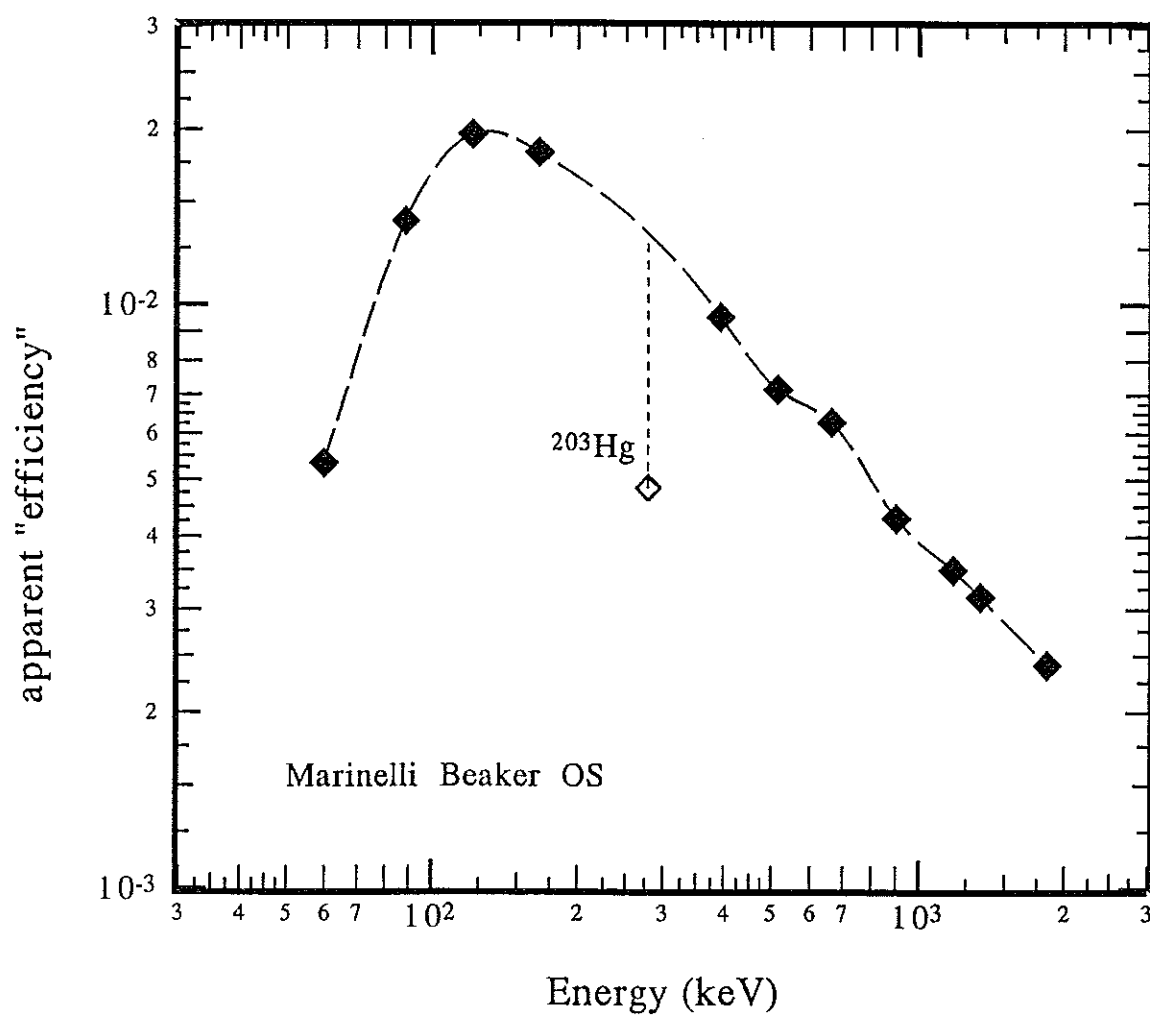
The spiking and preparation scheme that was developed for this work was demonstrated to be adequate. It provides a very good quantitative "handle" on the entire process, and has sufficient provisions for verifying possible spiking losses and assuring source homogeneity.

To a first cut, the Marinelli beaker source OS1 appears to have "worked" in the sense that the Ottawa sand was sufficiently adsorptive and that the spiking radionuclides, excepting ²⁰³Hg, were quantitatively transferred from the spiking master solution M1 to the sand to better than 99.5%.

Source homogeneity as determined from measurements on aliquants (30 g samples out of 1850 g of sand) was demonstrated to be within a few percent which is more than adequate for γ -ray spectrometry in a Marinelli-beaker configuration.

The calibration obtained in this work will now allow NIST to provide calibration services for other Marinelli beaker sources, provided that these sources are in the same geometry, use the same Ottawa sand matrix, and contain the same radionuclides.

Figure 4.
Calibration of the Marinelli-beaker calibration standard OS1
in terms of an apparent efficiency curve
as obtained with the NIST "T" detector



Annex A: Densities, particle-size distributions, and volume packing considerations for the mock "soil" matrices

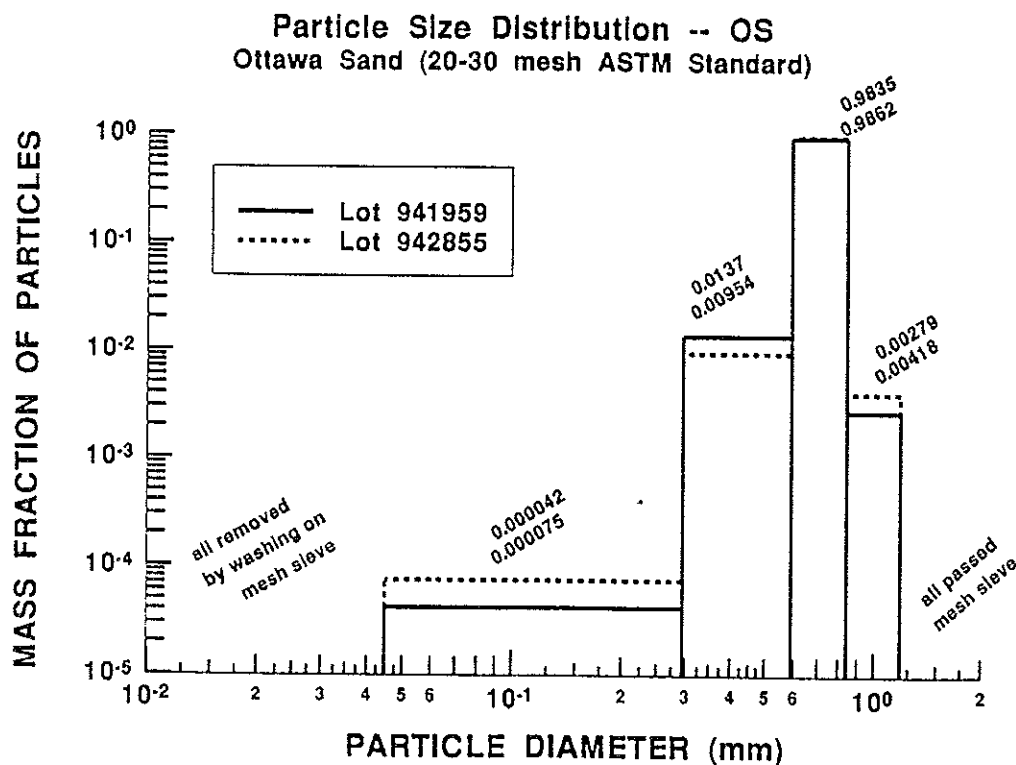
Standard Ottawa sand (OS)

Two lots of 20-30 mesh standard Ottawa sand, obtained from Fisher Chemical (S23-3) were examined. As a pretreatment, to remove very fine silica dust, the sand was washed with distilled water on a 325-mesh (0.045 mm) sieve and dried under an infrared heat lamp.

The bulk density was found to be $1.721 \text{ g}\cdot\text{cm}^{-3} \pm 0.006 \text{ g}\cdot\text{cm}^{-3}$ (adopt $1.72 \text{ g}\cdot\text{cm}^{-3} \pm 0.01 \text{ g}\cdot\text{cm}^{-3}$) where the cited uncertainty is a standard deviation with $\nu = 9$ for 10 independent mass determinations (with both lots) in volumes of 500 and 1000 cm^3 . The density largely depends on extent of granular packing (which in turn determines volume of a given mass). The density given was that obtained with moderate tapping and settling. Loosely packed density can be as low as $1.3 \text{ g}\cdot\text{cm}^{-3}$; and extreme packing as high as $1.76 \text{ g}\cdot\text{cm}^{-3}$.

Gravimetric determinations of particle size distributions for the washed sand were performed by screening through standard mesh screens and subsequent weighings of the fraction of sand retained on each screen. The particle size distribution may be characterized as $0.7 \text{ mm} \pm 0.1 \text{ mm}$ as follows: Figure A1 gives the particle size distribution for mass fraction of particles between various mesh-size sieves. Particles below 0.045 mm are excluded because they were removed by washing. No substantial differences between samples from two lots were observed. Over 98% of the mass have

Figure A1.



mean diameters between 0.59 mm and 0.84 mm. Figure A2 gives the distribution for the number fraction of particles which was calculated from the data of Figure 1 on the assumptions that the grain density of all particles is constant and independent of grain size and that the particles are spherical (or at least that the volume of the particles is proportional to the cube of the mean particle diameter). Obviously, in terms of number fraction there is an enhancement in smaller particles. Figure A3 shows a theoretically modelled particle size distribution (based on the data of Figure 2) obtained from assuming that the particle diameters are a truncated normal distribution. This distribution can be described in terms of parameters $\mu = 0.700$ mm and $\sigma = 0.097$. The slight discontinuities in the calculated distribution of Figure A3 are merely the result of numerical imprecision in the calculations.

The grain density was approximated to be roughly 0.00069 gram per average grain. This corresponds to $3.6 \text{ g}\cdot\text{cm}^{-3}$ assuming a spherical mean particle diameter of 0.7 mm -- the lower and upper limits are 2.2 and $6.4 \text{ g}\cdot\text{cm}^{-3}$ because of the wide range in particle diameters. The grain density estimate was obtained from mass measurements on three samples of 100, 100, and 50 grains (selected from the 0.59 mm to 0.84 mm size bin).

Based on the above average bulk density and grain density, the volume packing corresponds to roughly 64% of a maximum theoretical value ($1.72/3.6 = 0.48$ compared to 0.741, since at closest packing 0.259 of the total volume is occupied by void spaces in a large volume of spheres of equal radii). Density of various silica minerals range from $2.2 \text{ g}\cdot\text{cm}^{-3}$ to $2.7 \text{ g}\cdot\text{cm}^{-3}$. Using these as estimates of the grain density results in estimated volume packing of 106% and 86% of theoretical limits.

Figure A2.

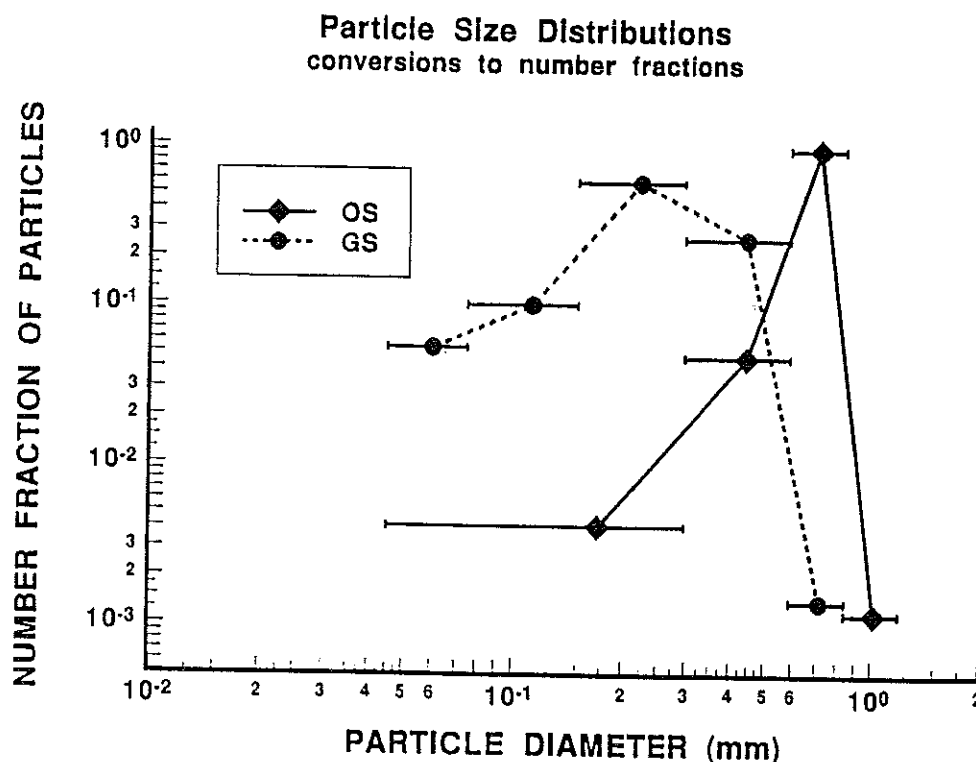
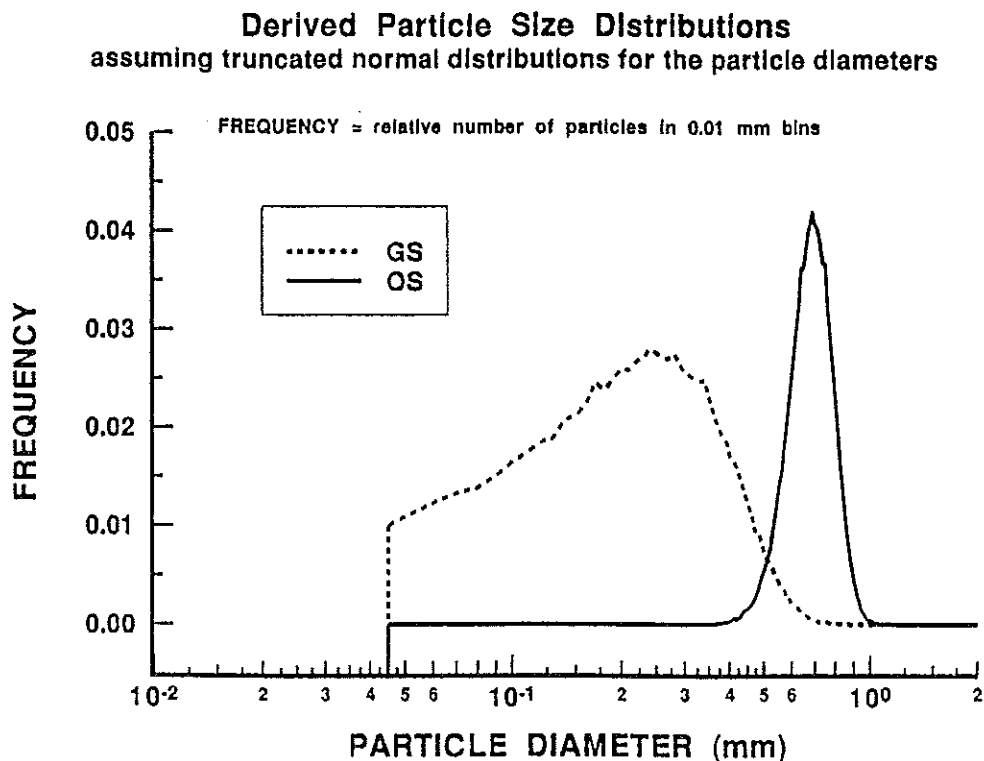


Figure A3.



Granular sodium chloride (GS)

This matrix was a USP/FCC granular sodium chloride, obtained from Fisher Chemical (S-640-10).

The bulk density was found to be $1.36 \text{ g}\cdot\text{cm}^{-3} \pm 0.02 \text{ g}\cdot\text{cm}^{-3}$ where the cited uncertainty is a standard deviation with $\nu = 5$ degrees of freedom for 6 independent mass measurements in volumes of 500 cm^3 and 1000 cm^3 . The density depends on packing, but is also more variable because of the water content of salt (extent of drying).

The particle size distribution may be characterized as $0.26 \text{ mm} \pm 0.15 \text{ mm}$ (fitted parameters). Figures A4 (mass fractions), A2 (number fractions), and A3 (modelled distribution) give results treated comparably as that above for OS. As indicated, the particle sizes of GS compared to OS are smaller, and more broadly distributed. It was unknown whether the salt would become finely pulverized during a blending process. Figure A4 gives the distributions before and after 2 hours of blending. There is no substantial difference in the two distributions indicating that powdering of the salt during blending is not a major concern.

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Figure A4.

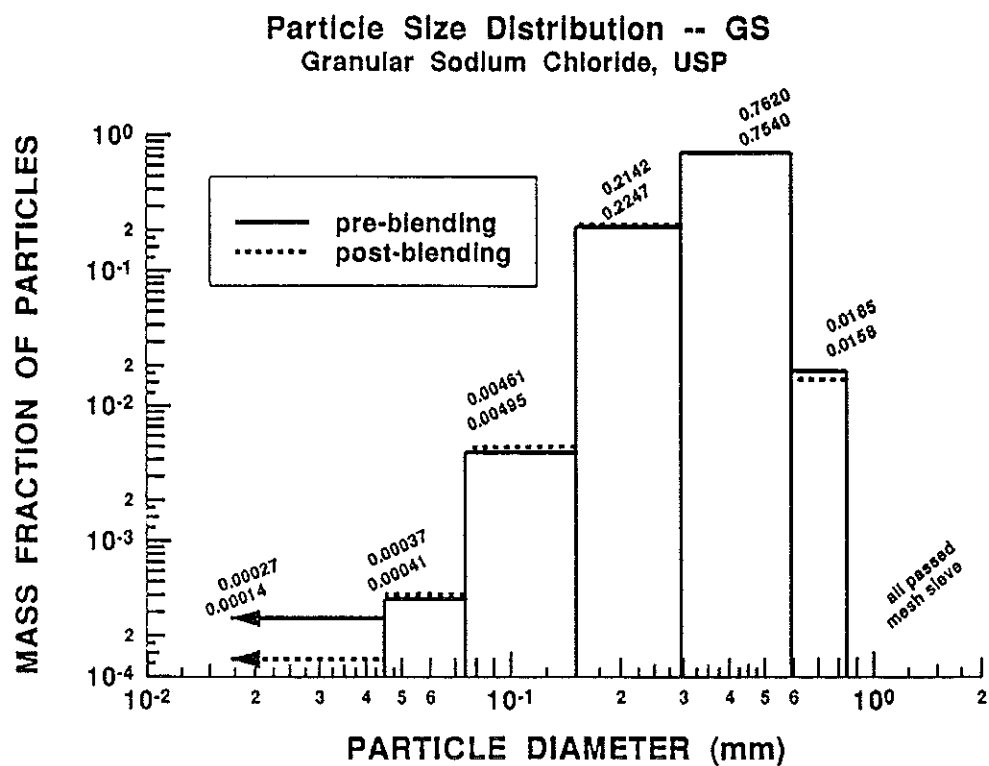


Figure 1.
 Schema for the spiking and preparation of the mock "soil"
 Marinelli beaker calibration standard.

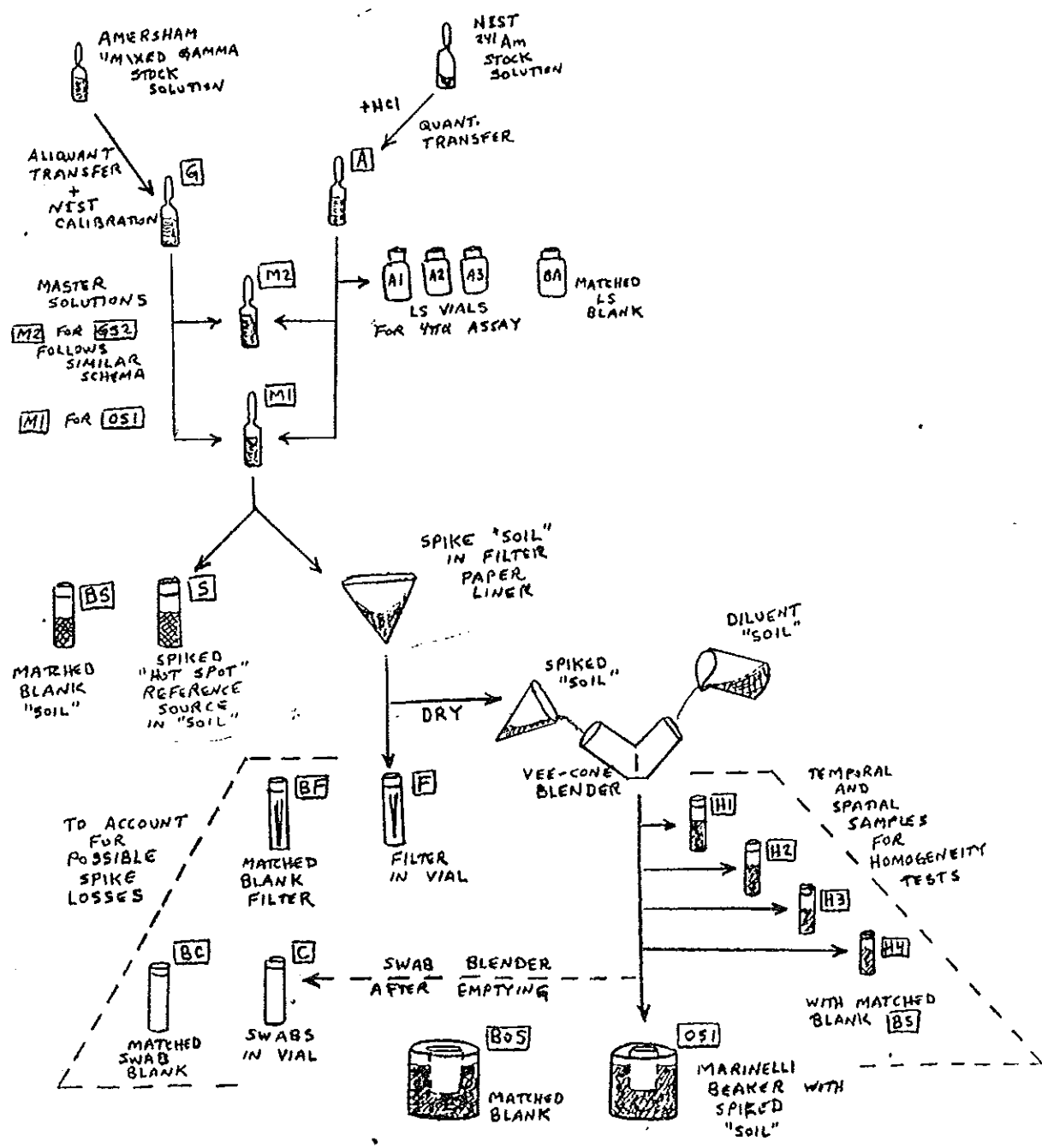


Table 3.

Homogeneity samples for preparation of OS1

sample	mass of sample (g)	blending time (min)
H1-OS	33.6888	40
H2-OS	32.5688	120
H3-OS	33.3162	244
H4-OS	30.9877	400

was no substantial fractionation of the radionuclides in the samples, excepting that for ^{203}Hg . These NaI(Tl) results were, of course, at best only semi-quantitative. The relative mean gross γ activity in the 4 homogeneity samples was, however, also in agreement to within about 0.5% with that expected from the total M1 solution mass spiked in the total OS mass.

Figure 2 gives the results of these gross γ activity measurements on the samples. The "homogeneity measure" given in the figure corresponds to the mass ratio M1/OS. This was obtained by normalizing the NaI(Tl) counting rate concentrations to that obtained from a known aliquant of M1 in OS (the "hot spot" spike -- see Figure 1). The displayed results are normalized values from 4 determinations obtained by integrating the full-energy NaI(Tl) spectra. The dotted line in Figure 6 is the gravimetrically determined M1/OS ratio.

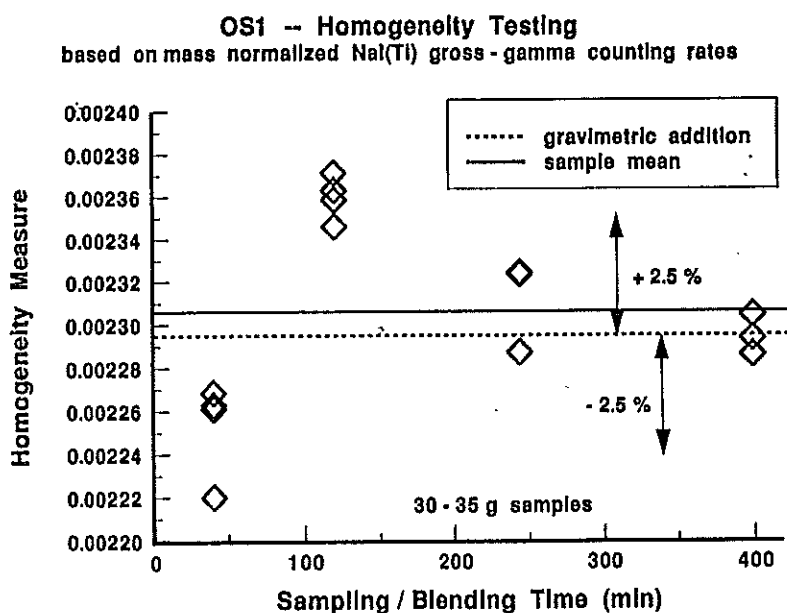
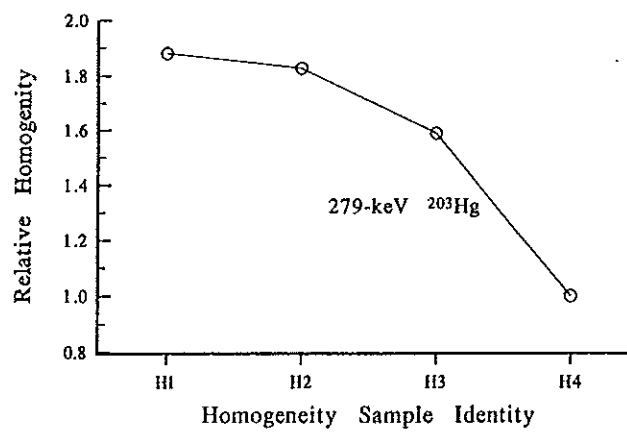
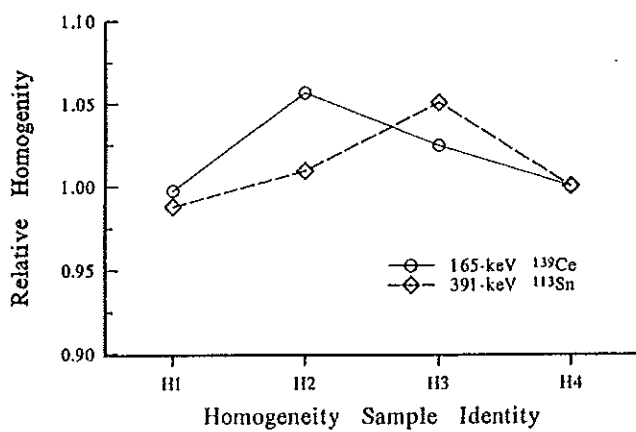
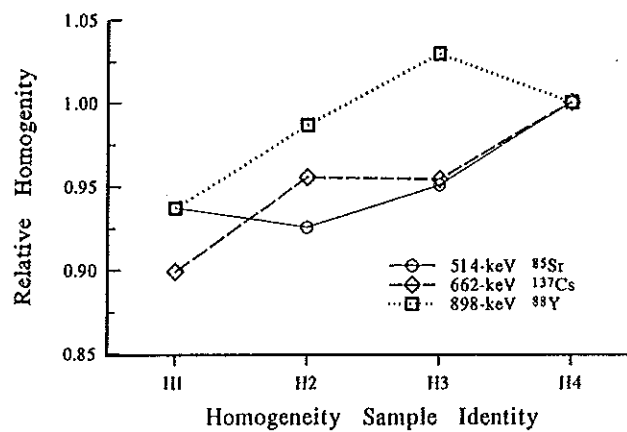
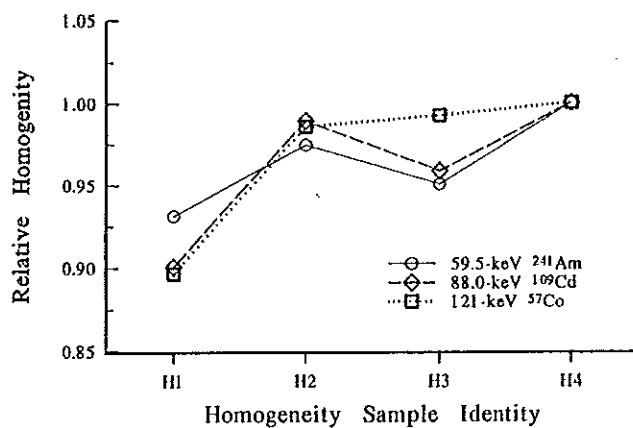


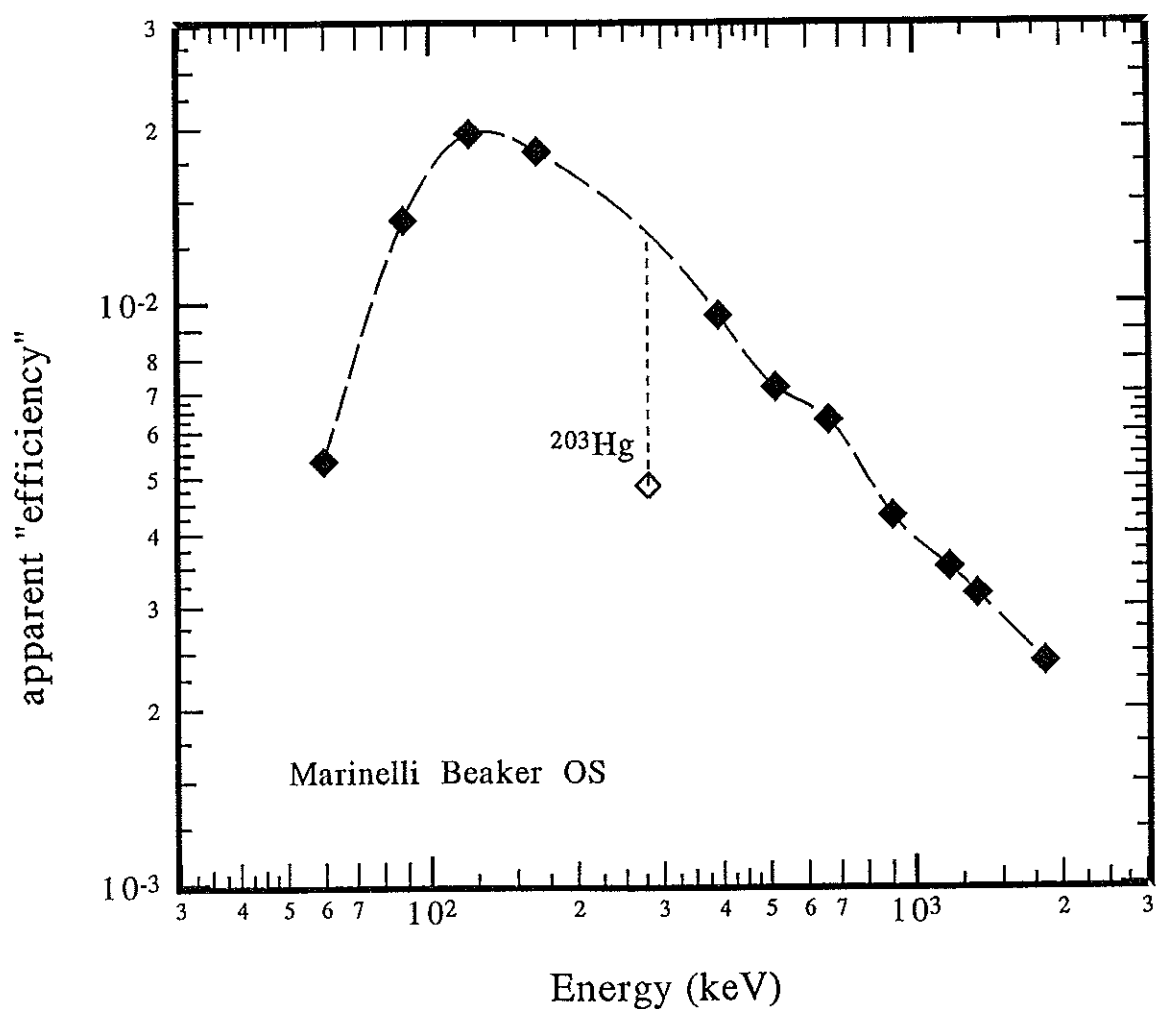
Figure 2.

Figure 3.
Relative homogeneity of the individual radionuclides in four aliquants
taken as a function of blending time (40 min to 400 min)
as measured with the high-resolution NIST "X" detector.



The calibration obtained in this work will now allow NIST to provide calibration services for other Marinelli beaker sources, provided that these sources are in the same geometry, use the same Ottawa sand matrix, and contain the same radionuclides.

Figure 4.
Calibration of the Marinelli-beaker calibration standard OS1
in terms of an apparent efficiency curve
as obtained with the NIST "T" detector



Annex A: Densities, particle-size distributions, and volume packing considerations for the mock "soil" matrices

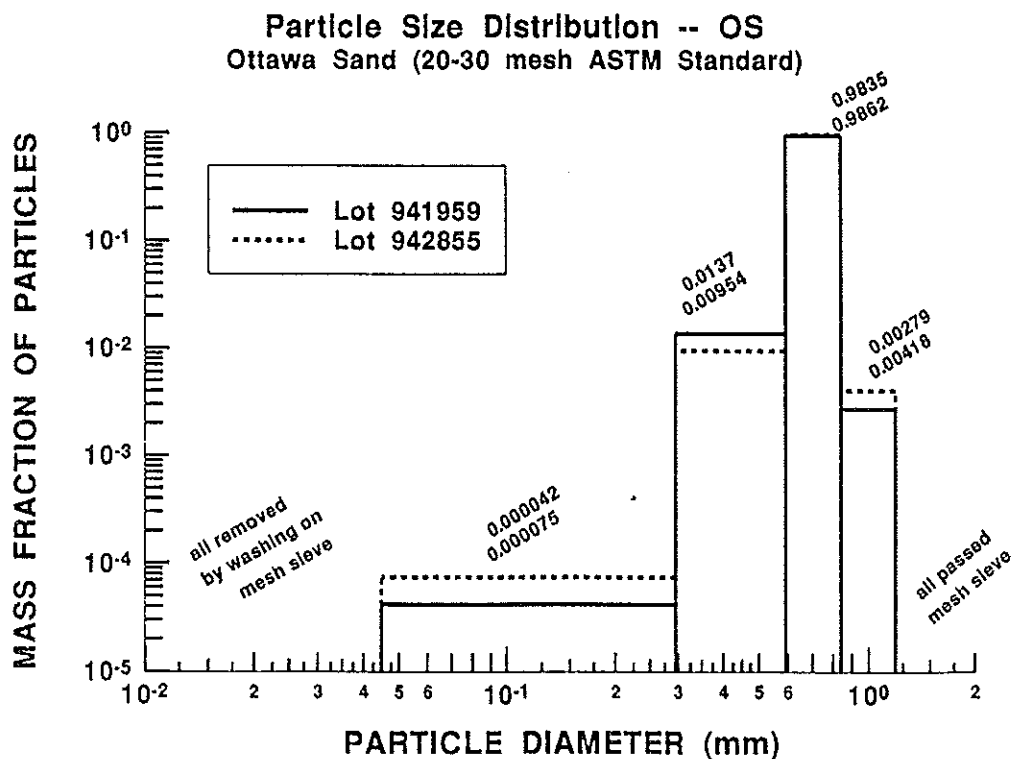
Standard Ottawa sand (OS)

Two lots of 20-30 mesh standard Ottawa sand, obtained from Fisher Chemical (S23-3) were examined. As a pretreatment, to remove very fine silica dust, the sand was washed with distilled water on a 325-mesh (0.045 mm) sieve and dried under an infrared heat lamp.

The bulk density was found to be $1.721 \text{ g}\cdot\text{cm}^{-3} \pm 0.006 \text{ g}\cdot\text{cm}^{-3}$ (adopt $1.72 \text{ g}\cdot\text{cm}^{-3} \pm 0.01 \text{ g}\cdot\text{cm}^{-3}$) where the cited uncertainty is a standard deviation with $\nu = 9$ for 10 independent mass determinations (with both lots) in volumes of 500 and 1000 cm^3 . The density largely depends on extent of granular packing (which in turn determines volume of a given mass). The density given was that obtained with moderate tapping and settling. Loosely packed density can be as low as $1.3 \text{ g}\cdot\text{cm}^{-3}$; and extreme packing as high as $1.76 \text{ g}\cdot\text{cm}^{-3}$.

Gravimetric determinations of particle size distributions for the washed sand were performed by screening through standard mesh screens and subsequent weighings of the fraction of sand retained on each screen. The particle size distribution may be characterized as $0.7 \text{ mm} \pm 0.1 \text{ mm}$ as follows: Figure A1 gives the particle size distribution for mass fraction of particles between various mesh-size sieves. Particles below 0.045 mm are excluded because they were removed by washing. No substantial differences between samples from two lots were observed. Over 98% of the mass have

Figure A1.



mean diameters between 0.59 mm and 0.84 mm. Figure A2 gives the distribution for the number fraction of particles which was calculated from the data of Figure 1 on the assumptions that the grain density of all particles is constant and independent of grain size and that the particles are spherical (or at least that the volume of the particles is proportional to the cube of the mean particle diameter). Obviously, in terms of number fraction there is an enhancement in smaller particles. Figure A3 shows a theoretically modelled particle size distribution (based on the data of Figure 2) obtained from assuming that the particle diameters are a truncated normal distribution. This distribution can be described in terms of parameters $\mu = 0.700$ mm and $\sigma = 0.097$. The slight discontinuities in the calculated distribution of Figure A3 are merely the result of numerical imprecision in the calculations.

The grain density was approximated to be roughly 0.00069 gram per average grain. This corresponds to $3.6 \text{ g}\cdot\text{cm}^{-3}$ assuming a spherical mean particle diameter of 0.7 mm -- the lower and upper limits are 2.2 and $6.4 \text{ g}\cdot\text{cm}^{-3}$ because of the wide range in particle diameters. The grain density estimate was obtained from mass measurements on three samples of 100, 100, and 50 grains (selected from the 0.59 mm to 0.84 mm size bin).

Based on the above average bulk density and grain density, the volume packing corresponds to roughly 64% of a maximum theoretical value ($1.72/3.6 = 0.48$ compared to 0.741, since at closest packing 0.259 of the total volume is occupied by void spaces in a large volume of spheres of equal radii). Density of various silica minerals range from $2.2 \text{ g}\cdot\text{cm}^{-3}$ to $2.7 \text{ g}\cdot\text{cm}^{-3}$. Using these as estimates of the grain density results in estimated volume packing of 106% and 86% of theoretical limits.

Figure A2.

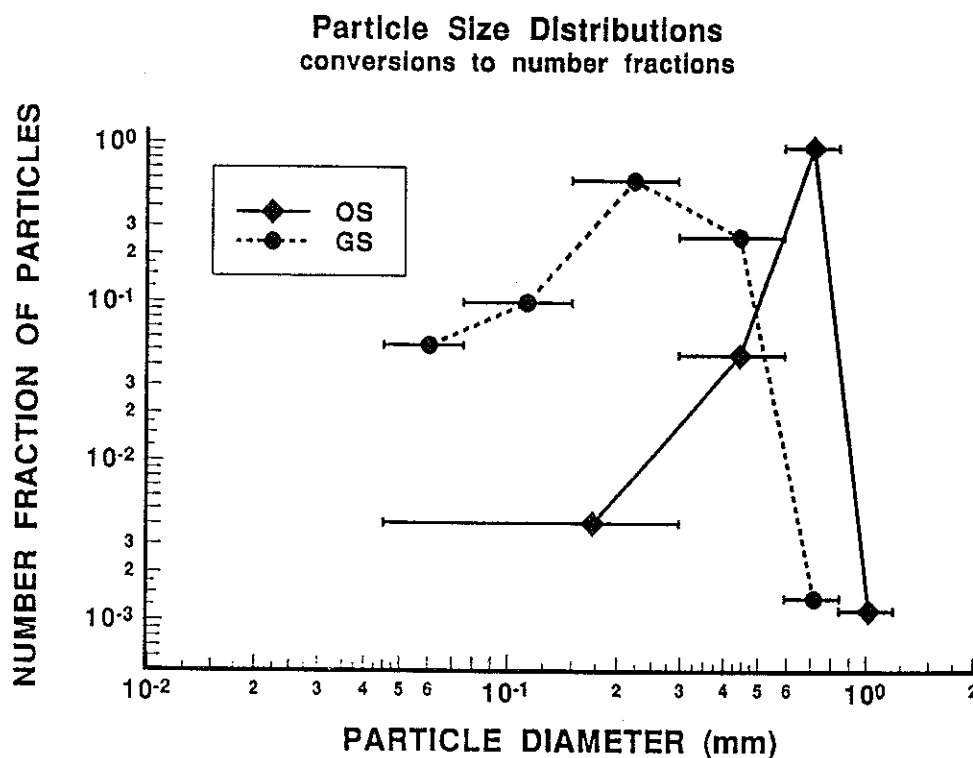
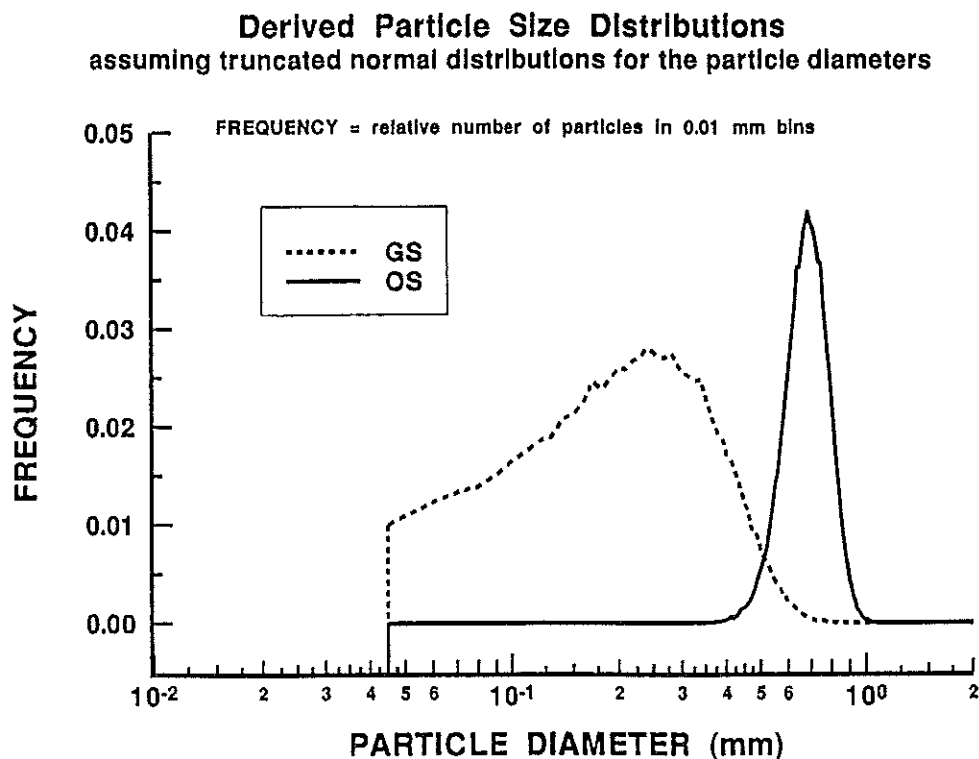


Figure A3.



Granular sodium chloride (GS)

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