to 9000 Å (for $v' = 0$), where the photocathode sensitivity is low and OH emission would interfere.

Table 1 shows the observed wavelengths of the principal new system, the $C^3\Delta_{1u} \rightarrow a^1\Delta_g$ bands, from which new spectroscopic constants for the $a^1\Delta_g$ state may be determined. Observed and calculated band intensities are also listed, on the assumption of a constant electronic transition moment. The calculated intensities are based on interpolations between sets of Franck-Condon factors calculated for the *A*-*a* and *c*-*a* transitions (*17*).

Now that it is known that there are easily observable transitions from the $A^3\Sigma_u^+$, $C^3\Delta_u$, and $c^1\Sigma_u^-$ states, it should be practical to carry out a variety of measurements. It is evident that all three states will be generated by recombination of O atoms in both the terrestrial and the venusian atmospheres. The fact that Earth's atmosphere shows principally *A*-*X* bands, whereas only *c*-*X* bands appear in the venusian nightglow, suggests that the difference lies in the quenching and relaxation kinetics of the two systems, as the peak O atom densities are not very different (*18*). Thus quenching rate coefficients by O atoms, O_2, N_2, and CO_2 are needed to clarify the emission features (it is already obvious that quenching of $c^1\Sigma_u^-$ by N_2 and CO_2 is very slow, whereas $C^3\Delta_u$ and $A^3\Sigma_u^+$ quenching by CO_2 is more rapid). Such data will also lead to relative values of the radiative lifetimes.

The O atom recombination into these energetic states of O_2 is likely to be an important process, and the difficulty in observing emission only reflects their weak radiative properties. It may be that both in the atmosphere and in combustion reactions these O_2 states play important roles. Furthermore, subsequent studies should establish significant details about the recombination process, such as the relative initial distribution among the electronic states and the efficiency of cross relaxation interactions.

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19. This work is dedicated to the memory of Prof. H. P. Broida, whose recent death has saddened his many friends in the scientific community. Herb was involved in the study of the O_2 metastable states from his classic publication in 1954 to the present time, and I acknowledge his enthusiastic encouragement during the course of the present work. I think that the outcome would have pleased him. I thank G. Black, D. L. Huestis, and R. P. Saxon for valuable discussions. I thank D. L. Albritton for providing me with calculations of the Franck-Condon factors. This work was jointly supported by NASA contract NASW-2849 and Army Research Office contract DAAG29-77-C-0018.

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Size Fractionation Methods: Measuring Plutonium in Respirable Dust

Abstract. *Methods used to evaluate the inhalation hazard of soil contaminated with plutonium were investigated. Four soil fractionation procedures were used to separate three size fractions of soil particles taken from two locations at the Department of Energy's Rocky Flats facility. The results show that increasing amounts of soil mass and plutonium activity (0.5 to 38 percent and 7 to 84 percent, respectively) remain in the fraction of soil smaller than 10 micrometers as the in situ particle associations are increasingly disrupted by physical and chemical forces. The introduction of forces of dispersion unrelated to ambient conditions yields results that are unrelated to the original particle associations.*

In the past, the purpose of most environmental surveys for plutonium in soil has been to establish the total inventory for a particular location. More recently, questions regarding the inhalation potential for contaminated soil have prompted investigators to recommend different methods of soil sampling and analysis to evaluate the inhalation potential. Unfortunately, the different methods recommended can yield conflicting results. For example, Tamura (*1*) recommended a procedure in which particle dispersion is minimal. His stated objective was to retain the association of the plutonium with the soil particles. On the other hand, Johnson *et al.* (*2*) recommended a procedure in which particle dispersion is maximized. Their stated objective was to disperse the soil microaggregates to expose the plutonium as much as possible. With such opposing objectives, dissimilar results can be expected.

The following study was initiated to establish the magnitude of the differences one might expect if one were to use four soil fractionation methods (described below) on two soil samples taken from the Department of Energy's Rocky Flats facility. The basis for the sample site selection was an observed difference in surface character and plutonium activity in the soil at the two locations. Sample 1 was taken from a site that was densely covered with prairie grasses. The surface soil was fine-grained and rich in organic litter. The plutonium activity at this site averages about 2 dpm/g as established by an analysis of surface core samples (10 by 10 by 5 cm deep) taken in the summer of 1975. Sample 2 was taken from a site that was nearer to the release point and sparsely covered by prairie grasses. The surface was rocky, and the soil was intermixed with many small pebbles. The plutonium activity at this site averages about 80 dpm/g, as determined by the same sampling technique.

I resampled these two sites in October 1976, using the collection method specified by Johnson *et al.* (*2*) (0.5-cm-deep surface sample). Each sample was field-sifted through a 10-mesh screen, yielding fractions larger and smaller than 2000 μm. Mass, moisture, and plutonium data were obtained from the two fractions. The fraction of each sample smaller than 2000 μm was separated into even smaller fractions (2000 to 37 μm, 37 to 10 μm, and < 10 μm) according to the following four methods.

Method A, dry sift. About 100 g of the < 2000-μm fraction were sifted through a series of screens to obtain the desired subfractions. A stack of vibrating screens was used to separate the larger particles (2000 to 37 μm). One gram of the 37-μm fraction was placed in an ultrasonic sifter on a 10-μm screen to separate the fraction between 37 and 10 μm (*3*).

Method B, sedimentation with minimal agitation [Tamura's procedure (*1*)]. Approximately 25 g of the < 2000-μm fraction were combined with 1600 ml of water and 15 mg of Aerosol OTB surfactant (American Cyanamide Company). The slurry was stirred with a glass rod. A sedimentation time of 65 seconds, and a fall of 8 cm, was used to separate the 37-μm fraction. A sedimentation time of 17 minutes and 20 seconds was used to separate the < 10-μm fraction. Separation was by decantation, and each separation was repeated four times. Water was removed by evaporation prior to analyses.

Method C, sedimentation preceded by ultrasonication. Approximately 25 g of the < 2000-μm fraction were placed in an ultrasonic bath with 300 ml of water and 15 mg of Aerosol OTB. The slurry was ultrasonicated for 2 hours at a power level of 40 W. The dispersed sample was then placed in a beaker and the volume was adjusted to 1600 ml with water. The sedimentation procedure described in method B was then used to separate the desired fractions.

Method D, sedimentation and ultrasonication preceded by hydrogen peroxide digestion [Johnson *et al.* method (*2*)]. Approximately 25 g of the < 2000-μm fraction was placed in a beaker containing 200 ml of water. The sample was warmed, and 100 ml of hydrogen peroxide was added in 10-ml increments. The excess peroxide was decomposed by slow evaporation to about 50 ml over 24 hours. The slurry was transferred to the ultrasonic bath where the volume was increased to 300 ml with water and treated as described in method C.

The < 2000-μm fraction of sample 1 contained 2.7 percent moisture and 69.5 percent of the total sample mass. The < 2000-μm fraction of sample 2 contained 1.6 percent moisture and 51.6 percent of the total sample mass.

The weight percentage of the < 2000-μm fraction of soil appearing in the < 10-μm subfraction of each sample is shown in Table 1. The percentage increases as the sample pretreatment becomes more rigorous. Method A yields five to ten times less mass in this fraction than method B. Such results are reasonable because the forces of adhesion, as described by Davies *et al.* (*4*), are significantly reduced in water, and the energy needed to detach particles from surfaces in water are less than one-tenth of that required in air. Similarly, when samples are pretreated according to methods C and D, the weight percentage of the soil appearing in the < 10-μm fraction increases. Thus the mass of material within this fraction changes relative to the method used.

Table 1. Weight percentages and total ^{239}Pu alpha activity in the < 10-μm subfraction for four fractionation methods.

Method	Weight percentage		^{239}Pu activity (dis/min)	
	Sample 1	Sample 2	Sample 1	Sample 2
A*	0.5	1.0		
B	5.5	5.4	6	163
C	31.0	14.3	93	1609
D	38.8	22.7	107	2492

*The amount of soil that could be placed on the 10-μm screen was limited to 1 g. The amount passing through the screen was insufficient for radiometric analysis. The sedimentation results are based on a 25-g sample.

The data in Table 1 also show an increase in the total amount of plutonium appearing in the < 10-μm fraction as the pretreatment becomes more rigorous. Thus the plutonium activity within this fraction also changes relative to the method used. The results indicate that < 10 percent of the plutonium [that is (in disintegrations per minute), 6/76 and 163/2318] is in the < 10-μm fraction if Tamura's method is used. With the procedure recommended by Johnson *et al.*, about 80 percent of the plutonium (107/144 and 2492/2981) was found in the < 10-μm fraction. The difference is due to the fact that with Tamura's method plutonium is evaluated in terms of its association with the soil; with the method of Johnson *et al.* the plutonium is evaluated after some degree of dissociation. Earlier data (*5*) on unassociated plutonium in soil at Rocky Flats, obtained by nuclear tracking techniques, indicate that the mean plutonium particle size is about 0.3 μm or less. Thus far, plutonium particles larger than about 2 μm have not been found in Rocky Flats soil. The results of the use of method D tend to support the nuclear tracking data in terms of particle size, but do not provide new or surprising information.

The three sedimentation procedures yielded an average cumulative plutonium concentration of 6 and 107 dpm/g in the < 2000-μm fraction samples 1 and 2, respectively. Considering the heterogeneity of a soil/plutonium particle system and the fact that the errors are additive when one is summing the separate soil fractions, these results compare reasonably well with values obtained in the summer of 1975 (sample 1, 2 dpm/g; sample 2, 80 dpm/g). This result indicates that the 0.5-cm-deep surface sample taken for this study did not yield results considerably higher than that previously obtained from the 5-cm-deep surface core. The higher plutonium activity values reported by Johnson *et al.* are due primarily to the different fractionation procedure rather than to the method of sampling.

The specific data reported above will not be representative of all contaminated soils. The data do illustrate that two dissimilar surface soils having different plutonium concentrations show similar trends in the changing content of the < 10-μm fraction, the change being highly dependent on the fractionation method used. The selection of the proper method depends on the objective of the work. If the objective is to estimate the amount of plutonium associated with the < 10-μm fraction of soil under ambient conditions, then method A provides an estimate for a totally dry situation and method B provides an estimate for a totally wet situation. Methods C and D introduce forces that are unrelated to environmental conditions and therefore are not appropriate. In my viewpoint, method B, which maintains particle associations, under wet conditions, provides the most realistic conservative data for evaluating an environmental inhalation hazard. Method D shows only that at least 75 to 85 percent of the plutonium can be dissociated from the larger soil particles, and that the particle size of the dissociated plutonium is less than 10 μm.

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