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## Evaluation of the Uranium Double Spike Technique for Environmental Monitoring

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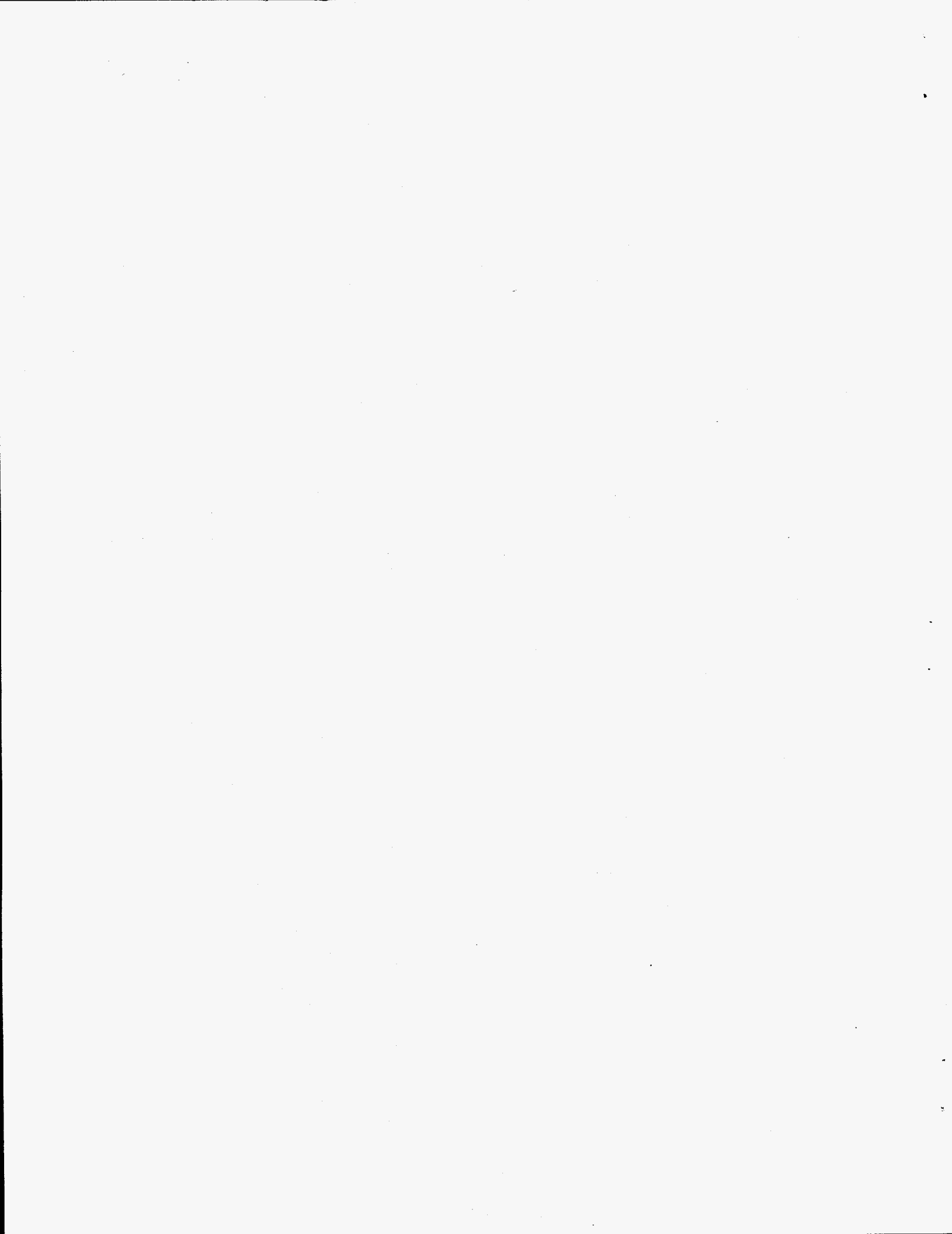
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## TABLE OF CONTENTS

<b>EXECUTIVE SUMMARY</b> .....	5
<b>1. INTRODUCTION</b> .....	7
<b>2. EXPERIMENTAL</b> .....	9
<b>2.1 CHEMISTRY</b> .....	9
<b>2.2 FILAMENT PREPARATION</b> .....	9
<b>2.3 INSTRUMENT</b> .....	10
<b>2.4 SPIKE PREPARATION AND ISOTOPIC DISTRIBUTION</b> .....	10
<b>2.5 CONCENTRATION MEASUREMENTS</b> .....	11
<b>2.6 SPIKE-TO-SAMPLE RATIO</b> .....	11
<b>3. ENVIRONMENTAL SAMPLES</b> .....	15
<b>4. CONCLUSIONS</b> .....	19
<b>5. RECOMMENDATIONS</b> .....	21
<b>6. ACKNOWLEDGEMENTS</b> .....	23
<b>REFERENCES</b> .....	25



## EVALUATION OF THE URANIUM DOUBLE SPIKE TECHNIQUE FOR ENVIRONMENTAL MONITORING

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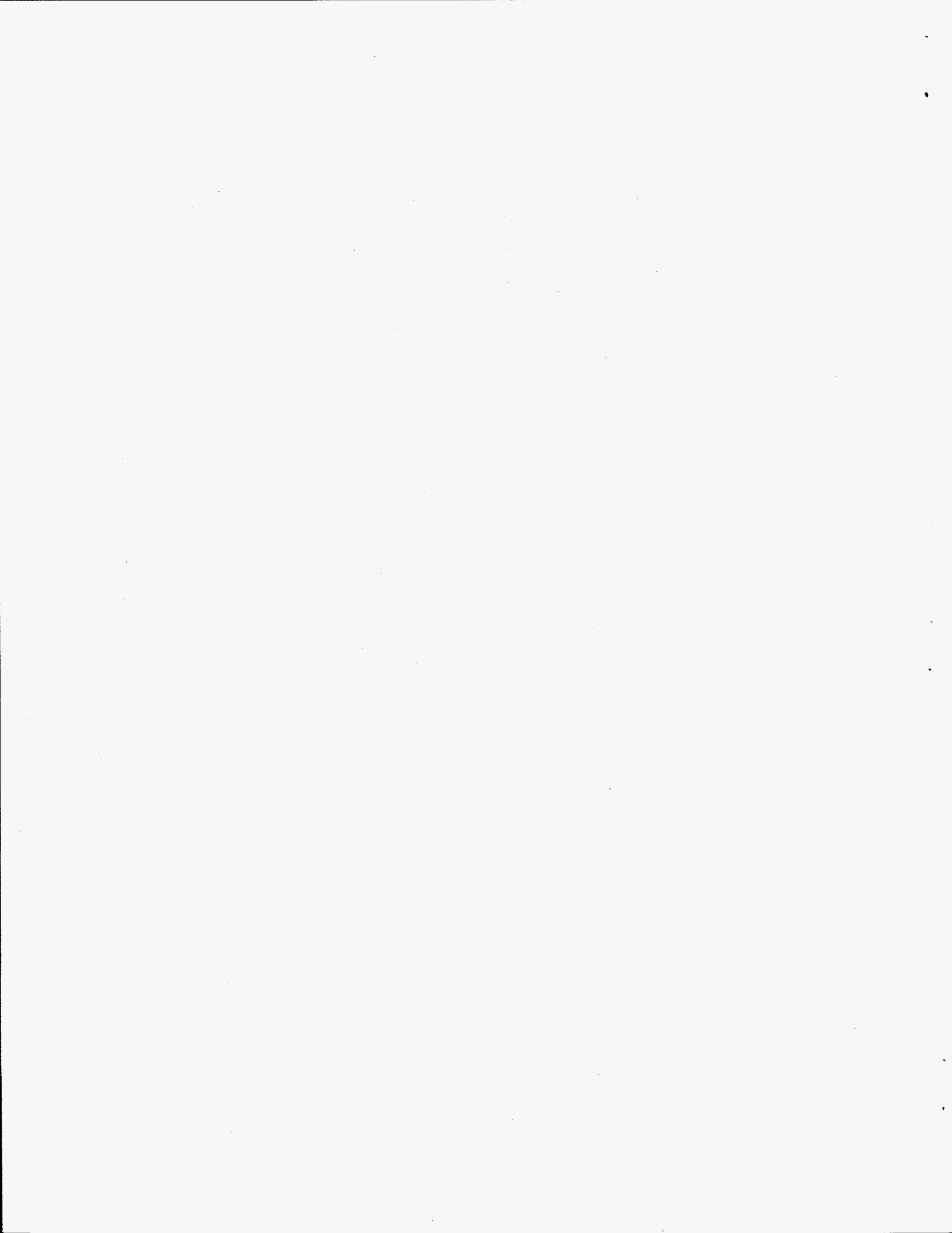
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### EXECUTIVE SUMMARY

Use of a uranium double spike in analysis of environmental samples showed that a  $^{235}\text{U}$  enrichment of 1% ( $^{235}\text{U}/^{238}\text{U} = 0.00732$ ) can be distinguished from natural ( $^{235}\text{U}/^{238}\text{U} = 0.00725$ ). Experiments performed jointly at Los Alamos National Laboratory (LANL) and Oak Ridge National Laboratory (ORNL) used a carefully calibrated double spike of  $^{233}\text{U}$  and  $^{236}\text{U}$  to obtain much better precision than is possible using conventional analytical techniques.

A variety of different sampling media (vegetation and swipes) showed that, provided sufficient care is exercised in choice of sample type, relative standard deviations of less than  $\pm 0.5\%$  can be routinely obtained. This ability, unavailable without use of the double spike, has enormous potential significance in the detection of undeclared nuclear facilities.





## 1. INTRODUCTION

One of the challenges facing nuclear safeguards today is that of detecting undeclared nuclear activities. There are two scenarios in which such an operation can be envisioned. One is when the undeclared activity is carried out at a known nuclear facility ostensibly serving a different function. The second is when the undeclared activity is being carried out at a location unknown to inspectors. It is this second scenario that the present experiment addresses.

Any nuclear operation leaves its signature in its immediate neighborhood. Some uranium escapes from an enrichment or other facility and leaves evidence of its presence in the form of an isotopic composition altered from that of the naturally occurring element. Any significant deviation from the natural  $^{235}\text{U}/^{238}\text{U}$  ratio is due to nuclear activity, and it is desirable to make the deviation defined by "significant" as small as possible. All rocks and soils contain uranium; it is present at the 3 part-per-million (ppm) level in the Chattanooga shale that covers much of the eastern United States, for example. Hence, once one is removed a few kilometers from a facility, natural uranium is present in far larger amounts than the anthropogenic uranium of interest. It, thus, becomes important to detect extremely small deviations from natural isotopic composition. Thermal ionization mass spectrometry is the method of choice in this application.

The purpose of this experiment was to evaluate the application of a uranium double spike to the measurement of the  $^{235}\text{U}/^{238}\text{U}$  ratio in environmental samples. Conventional isotopic analysis by thermal ionization mass spectrometry, while sensitive enough, does not provide sufficient reproducibility of measurement, being on the order of  $\pm 1\%$  ( $1\sigma$ ) for environmental samples of nanogram size with uranium having an isotopic composition near normal. This is due to a wide variety of causes that manifest themselves as isotopic fractionation that varies from one sample to the next in a manner impossible to control. It has long been known that use of an accurately known isotope ratio to correct for bias (fractionation) during analysis yields significant benefits. This method, known as internal calibration or double spike, involves comparing the measured value of the calibration ratio to the known and calculating the correction factor necessary to bring them into agreement. It is usually done on a run-by-run basis, so, as the fractionation rate varies during the course of an analysis, a new correction factor is calculated that accommodates it. It is of particular value when single-collector mass spectrometers are used. Because only one isotope at a time is monitored, fluctuations in ion beam intensity seriously degrade the quality of the results. Single-collector instruments are almost universally used in applications such as the one under consideration here because they can be equipped with pulse-counting detection systems. This gives them sensitivity superior to multi-collector instruments (ng vs.  $\mu\text{g}$  sample size) because technology has not yet developed to the point of making pulse counting viable in multi-collector arrays.

The internal calibration method has long been used in geological applications, where, for example, the  $^{86}\text{Sr}/^{88}\text{Sr}$  ratio (constant in nature) is used to determine the bias necessary for measurement of the  $^{87}\text{Sr}/^{88}\text{Sr}$  ratio (affected by radiogenic  $^{87}\text{Sr}$ ).<sup>1</sup> Dietz, et al., were the first to propose use of internal calibration through addition of a double spike to the sample.<sup>2</sup> It has been applied to molybdenum and nickel<sup>3</sup> and to uranium.<sup>4,5</sup> The theory behind its use has been described by Dodson.<sup>6,7</sup> It has not, to the authors' knowledge, ever been evaluated in a systematic manner for environmental monitoring of nuclear facilities. This application presents a tough problem to the analyst.

Samples are extremely small (in the nanogram range); they are messy and fraught with interferences of many kinds; preparatory chemistry must be meticulously executed in a clean environment.

It is important to understand what the double spike technique will do and what it won't. It will improve external precision and accuracy; it will not improve internal precision. External precision and accuracy are improved because calculation of bias correction factors specific to the analysis in question force the value of the target ratio to its proper value. The use of average bias is subject to many effects difficult or impossible to control, which leads to more scatter in the results. Internal precision, in contrast, is still subject to the same statistical variation in the ratio as conventional analyses; on a theoretical basis, ratios subjected to internal calibration should have somewhat poorer internal precision than those calculated conventionally because a correction must be applied to the sample peaks to subtract contributions from the spike. One of the major advantages, at least in principle, of using a double spike is that it should make accuracy (but not precision) independent of the laboratory. The reason accuracy becomes independent of the laboratory is because each laboratory uses the same spike and agrees upon its isotopic composition. Calibration is thus performed on the same basis in each laboratory with all measurements referred to the same reference ratio. The normal practice of using an average bias correction is the basis of much of the disagreement common in inter-laboratory comparisons. Whenever the double spike technique is used, all factors affecting bias, which vary between laboratories, are accumulated into one correction factor; the origins and magnitudes of the individual contributions do not matter.

To use a double spike, it is necessary to have two isotopes of the analyte element available for the purpose. They can be present in the sample itself, as in strontium, xenon, and krypton, or they can be added to the sample as a spike, as has been done with uranium and plutonium.<sup>8</sup> To reduce uncertainties introduced by corrections, it is highly desirable for the spike isotopes either to be absent or present in very low abundance in the sample itself. It is likewise desirable that the spike not contain the isotopes of concern at levels high enough to degrade analysis. It is for this reason that 233 and 236 are the isotopes of choice for uranium. Neither isotope occurs in nature and, though both can be present as the result of nuclear activity, neither is present at worrisome concentrations in the scenarios where highly accurate and precise measurement of  $^{235}\text{U}/^{238}\text{U}$  ratio is sought. Because uranium enriched in  $^{235}\text{U}$  is used both in weapons and in power reactors, it is this ratio that is the parameter of most importance to safeguards, either in verification of an existing operation or in detection of an undeclared one.

The goals of this experiment were, first, to prove that the double spike technique can reliably detect enrichment at the 1% level. This does not mean distinguishing a  $^{235}\text{U}$  abundance of 1% from natural; it means distinguishing between  $^{235}\text{U}/^{238}\text{U}$  ratios of 0.00725 (natural) and 0.00732 (1% enriched). We also wanted to evaluate the effect of sample-to-spike ratio on the results. A variety of sample types was analyzed to investigate the effect of sample matrix.

## 2. EXPERIMENTAL

### 2.1 CHEMISTRY

LANL and ORNL chemically processed the samples analyzed in this study by two separate protocols. LANL conducted studies to determine the effectiveness of using total sample dissolution techniques. ORNL conducted studies to determine the effectiveness of using nitric acid leaching techniques to separate the uranium from the samples.

The total sample dissolution, uranium separation, and purification procedures used by LANL have been described previously.<sup>9,10</sup> The cloth swipes analyzed for this study were wet ashed with a mixture of nitric acid and perchloric acid. The vegetation samples were autoclaved, dried in an oven at 110°C, and ashed in a muffle furnace at 550°C. The residues were then dissolved in strong mineral acids. The uranium fraction from each sample was purified by ion exchange chromatography. Ultra-pure acids produced by sub-boiling distillation were used throughout the sample dissolution and uranium purification procedures to minimize the uranium sample processing blanks.<sup>11</sup> All chemical processing was conducted in class-100 clean areas constructed according to the designs developed by the National Institute of Standards and Technology (formerly called the National Bureau of Standards).<sup>12</sup> All sample preparation and filament loading at LANL were carried out in class-100 clean areas.

ORNL leached weighed quantities of each sample in 4 M HNO<sub>3</sub>. The 4 M HNO<sub>3</sub> acid solutions containing the uranium leached from the samples were filtered and a known amount of <sup>233</sup>U tracer was added to an aliquot of each acid solution to determine the uranium content. The results from the <sup>233</sup>U spiking experiments were used to determine the amount of <sup>233,236</sup>U double spike added to the aliquots analyzed for the double spike experiments. The aliquots selected for the double spike experiments were spiked with the <sup>233,236</sup>U double spike and the samples were evaporated to dryness. The samples were re-dissolved in nitric acid and the uranium was isolated using UTEVA ion exchange columns from Eichrom Corporation. All sample preparation and filament loading at ORNL was carried out in a clean laboratory.

There are distinct advantages and disadvantages associated with both the total sample dissolution technique and the nitric acid leaching technique. The total sample dissolution technique is the method of choice if the uranium is suspected to be dispersed throughout the sample. The total dissolution technique requires more reagents than the nitric acid leaching technique. Hence, the uranium blank added to the sample during processing using total dissolution techniques is greater than the uranium blank added to the samples that are prepared by leaching techniques. The leaching technique removes the uranium from the surface of the samples. It is the chemical processing technique of choice for samples having only surface contamination.

### 2.2 FILAMENT PREPARATION

LANL co-plates uranium and platinum onto rhenium filaments and then overplates the uranium-platinum deposit with platinum to form surface ionization, diffusion-controlled sources. The technique was originally developed for plutonium analyses<sup>13</sup> and has been modified for uranium analyses.

At ORNL the purified uranium samples were loaded on anion resin beads, with a single bead used for each filament loading. This method of loading provides superior ion emission characteristics in comparison to loading solutions directly on the filaments.<sup>14</sup>

### 2.3 INSTRUMENT

The mass spectrometers employed at the two laboratories were functionally equivalent but differed in detail. Both laboratories use pulse-counting detection systems, which register each ion individually when it strikes the first dynode of the electron multiplier. Dead times were 10 and 27 nsec for ORNL and LANL, respectively. Linear bias correction was used at both laboratories. Bias arises from a number of different sources which are experimentally extremely difficult to isolate. A linear approximation is valid when a limited mass range is to be swept.

At LANL the samples were analyzed using a 12 in. radius, 90° magnetic sector thermal ionization mass spectrometer with pulse counting detection in a clean laboratory. Isotopic data were collected in blocks of 4 using magnetic field peak switching; typically 6 blocks of data were collected for <sup>233</sup>U, <sup>235</sup>U, <sup>236</sup>U, and <sup>238</sup>U, and 2 blocks of data for <sup>234</sup>U and <sup>236</sup>U. These blocks of data were individually corrected using the double spike correction factor calculated by the computer during data acquisition, then averaged to obtain the final value of the <sup>235</sup>U/<sup>238</sup>U ratio.

The ORNL mass spectrometer was designed and built at ORNL some decades ago.<sup>15</sup> The instrument has three stages in tandem: two 30-cm radius magnetic fields followed by a 43-cm radius electrostatic analyzer. The ion source high voltage is swept to effect mass scanning. Because this causes ions of different masses to experience different draw-out fields, bias is introduced in addition to that present when magnetic field scanning is employed. The average bias per mass in these studies, as measured by the double spike, was 0.437%/mass. This is somewhat higher than usual (normally bias is about 0.3%/mass), but this value varies considerably with individual multipliers. Only peak tops were monitored during data-acquisition. The number of times a single isotope was swept during a single traversal of the mass spectrum was adjusted to improve counting statistics. Uranium-238 was swept once during each cycle, <sup>233</sup>U and <sup>236</sup>U were swept twice, and <sup>235</sup>U swept four or eight times. Internal calibration correction for bias was applied on a run-to-run basis during data processing. As with LANL, individual runs were averaged to obtain the final value for <sup>235</sup>U/<sup>238</sup>U ratio.

### 2.4 SPIKE PREPARATION AND ISOTOPIC DISTRIBUTION

The spike was prepared at Los Alamos National Laboratory. Solutions containing known quantities of isotopically pure <sup>233</sup>U and <sup>236</sup>U were mixed to produce the <sup>233,236</sup>U double spike used in these experiments. The double spike was characterized both at LANL and at ORNL. Analysis of the LANL and ORNL data showed no significant differences in the isotopic results for the double spike. The data were pooled and averaged; the isotopic composition is given in Table 1:

Table 1. Isotopic Composition of the  $^{233,236}\text{U}$  Double Spike

Isotope	Abundance, atom %
233	47.1754
234	0.0111
235	0.5878
236	51.4601
238	0.7653
233/236 ratio	0.9167

At LANL, two separate samples of the double spike material were analyzed using the NBS 12/90 mass spectrometer in pulse counting mode to obtain the isotopic abundance. Each sample was analyzed by a different operator. These results were statistically indistinguishable; these data were therefore pooled together and treated as one set of data. The  $^{233}\text{U}/^{236}\text{U}$  ratio was also measured using simultaneous measurement of  $^{233}\text{U}$  and  $^{236}\text{U}$  in Faraday collectors using a VG 354 thermal ionization mass spectrometer. In these experiments, the  $^{233}\text{U}/^{236}\text{U}$  ratio was measured using the NIST U-500 standard for internal bias correction and then using a correction factor with no internal calibration. Here again, the difference in these two sets of results is statistically insignificant and the individual results were pooled to provide an average  $^{233}\text{U}/^{236}\text{U}$  ratio.

ORNL used the  $^{235}\text{U}/^{238}\text{U}$  ratio in NIST U-500, a certified isotopic standard, for internal calibration to determine the value of the  $^{233}\text{U}/^{236}\text{U}$  ratio in the spike; this value was then used as an internal calibration ratio to calculate its full isotopic composition.

## 2.5 CONCENTRATION MEASUREMENTS

At LANL the  $^{233,236}\text{U}$  double spike was added to known amounts of two different gravimetrically prepared dilutions of Standard Reference Material U-960 to determine the concentration of the double spike solution. Four samples (two from each dilution of the NIST U-960) were analyzed at Los Alamos using the NBS 12-90 mass spectrometer. The concentration of uranium in the spike was determined to be:  $[5.466 \pm 0.0039] \times 10^{14}$  atoms U/gram solution.

## 2.6 SPIKE-TO-SAMPLE RATIO

The relatively high abundance of  $^{235}\text{U}$  in the spike (nearly 0.6%) required consideration; application of the equations used in the double spike procedure requires correction of the 235 mass position for contribution from the spike to isolate the  $^{235}\text{U}$  contribution from the sample. It is highly desirable to use an amount of spike that does not degrade the analysis by necessitating too large a correction to  $^{235}\text{U}$ .

LANL performed experiments to determine if historical results from the analyses of previous Field Trial samples could be used to estimate the amount of double spike that is required for optimum results. The goal was to determine if prior knowledge of process could be used to determine spike levels and consequently reduce the cost of analysis. LANL used the same amount of spike (20 ng) for each

sample based on a nominal sample weight of approximately 100 ng of U. This led to a spike/sample ratio of *ca.* 1/5 (weight/weight), the rationale being to limit the contribution of  $^{235}\text{U}$  from the spike to 10% - 20% of  $^{235}\text{U}$  from the sample. However, the high variability of uranium in the samples caused the spike/sample ratio to vary considerably. Therefore, we conclude that the double spike technique can only be utilized to its fullest extent to detect anthropogenic uranium in vegetation and cloth swipe samples after an aliquot of the sample has been traced with  $^{233}\text{U}$  and analyzed to estimate its uranium content.

ORNL spiked the samples first with high purity  $^{233}\text{U}$  (99.9686%) to obtain the amount of U in the sample because of the variability in spike/sample ratio resulting from a fixed amount of spike. Using the estimate of concentrations from these measurements, the appropriate amount of the double spike was added to each sample. ORNL used an iterative reweighted Poisson regression technique<sup>16</sup> to estimate the optimum spike-to-sample ratio. This was determined to be about 1/6 (weight/weight); for this specific spike, a spike-to-sample ratio of 1/6 corresponds to a  $^{233}\text{U}/^{238}\text{U}$  ratio of about 0.08 for natural uranium. The validity of this value was tested by analyzing NIST U-950 with the  $^{233}\text{U}/^{236}\text{U}$  double spike at various spike/sample ratios. The results are summarized in Table 2. Four different spike/sample ratios were used: 1/1.2; 1/2.4; 1/4.8; and 1/9.6. Each spike/sample mixture was measured from at least three different filaments. Data were taken at two different count rates from most filaments; a full analysis (10 runs) was first performed at a count rate that exceeded  $1 \times 10^5$  counts per second  $^{238}\text{U}$ ; a second full analysis was then taken at a nominal  $5 \times 10^4$  counts per second  $^{238}\text{U}$ . Filament loadings were 20-40 ng U.

Table 2. NIST U-950 with Double Spike

Spike/sample	n*	Count Rate**	235/238	SD (1 $\sigma$ )	% RSD	233/238
1/1.2	3	3e+05	0.007215	0.000017	0.24	0.3700
	4	5e+04	0.007235	0.000036	0.50	0.3703
1/1.4	3	3e+05	0.007253	0.000012	0.17	0.1890
	3	5e+04	0.007246	0.000013	0.18	0.1889
1/4.8	5	3e+05	0.007245	0.000014	0.19	0.0930
	5	5e+04	0.007247	0.000029	0.40	0.0929
1/9.6	4	2e+05	0.007246	0.000019	0.26	0.0471
	3	5e+04	0.007245	0.000017	0.23	0.0472
All samples	30		0.007242	0.000021	0.29	
All but 1/1.2	24		0.007247	0.000017	0.23	
E5 w/o 1/1.2	12	XE5	0.007247	0.000014	0.19	
E4 w/o 1/1.2	12	5e+04	0.007246	0.000020	0.28	

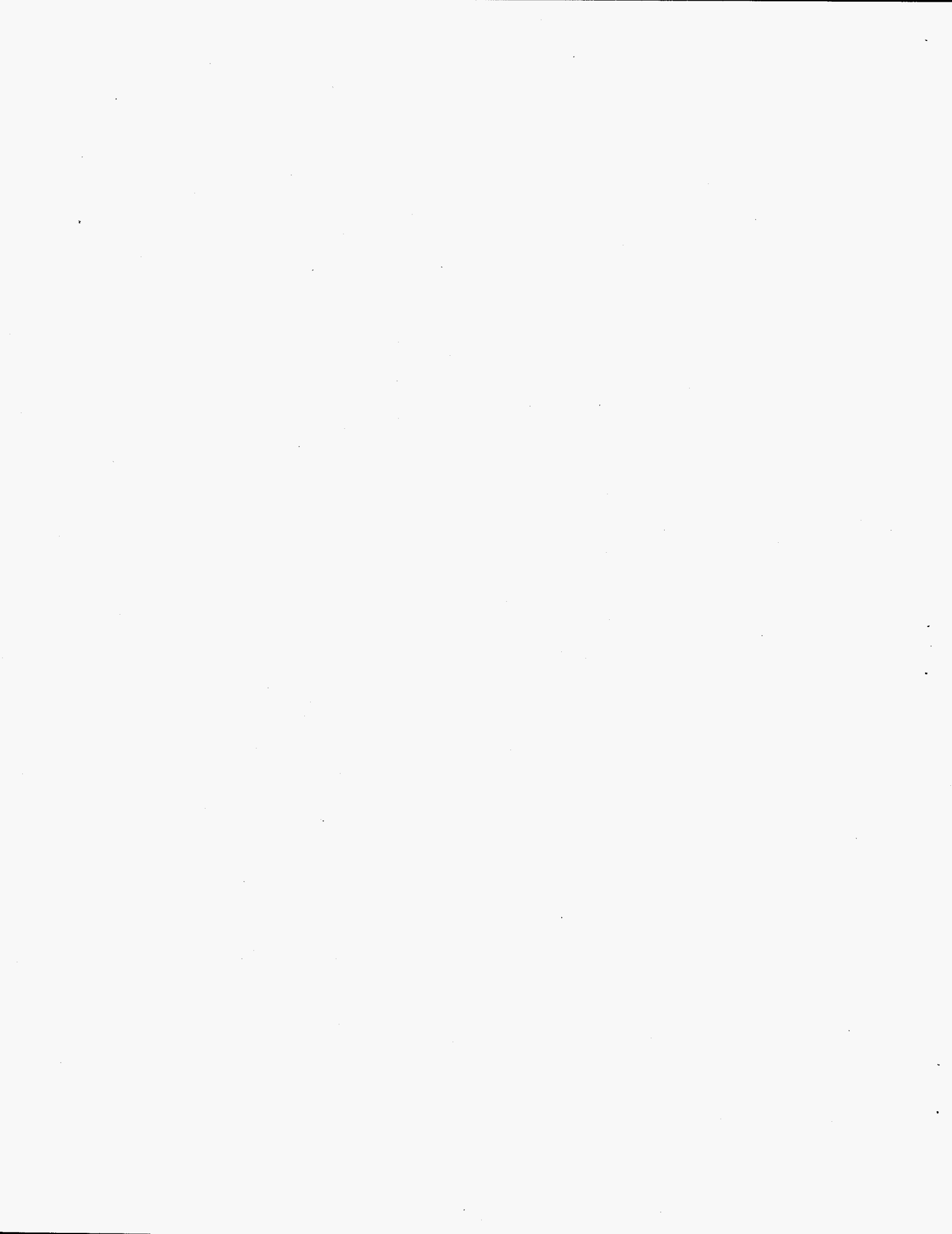
\* The number of replicate loadings analyzed.

\*\* Count rate of  $^{238}\text{U}$  in counts/sec.

All groups of analyses comfortably met the desired target of providing better than 1% accuracy. It is clear, both intuitively and from the data, that a spike/sample ratio of 1/1.2 is not optimum. In this situation the contribution of the spike to  $^{235}\text{U}$  is almost as great as that of the sample and represents a disadvantageous analytical situation; it is highly undesirable to have corrections approach the size of the signal of interest. All other spike/sample ratios gave results that are statistically indistinguishable. As expected, the higher count rate gave better results than the lower, but the results in Table 2 suggest that the penalty for a lower-than-optimum count rate is not great. This matter will be discussed in more detail in a later section.

The conclusion we draw from the results presented in Table 2 is that, although a spike/sample ratio of 1/6 may be optimum for this particular spike, there is a range of values for which viable results may be obtained.





### 3. ENVIRONMENTAL SAMPLES

Samples were provided from those collected during IAEA field trials. Each laboratory received different samples because the amounts remaining were insufficient to give both laboratories the same sample. Direct comparison of inter-laboratory results was not possible, both because of the limited amount of sample available and the inherent inhomogeneity of environmental samples. Samples were chosen to reflect a wide range of matrices. These included pine needles, deciduous leaves, bark, moss, and swipes. Table 3 lists LANL results. Because LANL ran each sample only once (one filament), Table 3 shows a comparison of the  $^{235}\text{U}/^{238}\text{U}$  ratio obtained with no double spike but using an average bias correction of 0.11%/mass to that obtained using the double spike for fractionation correction. The bias is the percent difference between the  $^{235}\text{U}/^{238}\text{U}$  ratio from the sample only (no spike) and the sample with the double spike. For all samples except PO-51 and PK-51, count rates handily exceeded  $10^5$  cps for  $^{238}\text{U}$ . No clear conclusions can be drawn from these data. However, the results in Table 3 tend to support the conclusion above from the U-950 study that viable results may be obtained from a range of spike/sample ratios. Please also note that the poorest agreement between the unspiked and spiked results was observed in those samples which were respiked, *i.e.*, additional spike was added to samples which were already spiked. There is a simple reason why this was done: there was no remaining unspiked sample from which a new spiked sample could be prepared. These results further document the necessity of measuring the amount of uranium in the sample prior to adding the  $^{233,236}\text{U}$  double spike.

Table 3. LANL Results from Environmental Samples

Sample	(235/238)u*	(235/238)ds**	RPD***	233/238	Type
PO-03	0.042665	0.043652	-2.28574	0.000245	Moss
PO-13	0.019571	0.019590	-0.09535	0.000619	Moss
PO-13R*		0.019813	-1.231	0.068353	Moss
PO-15	0.041674	0.041905	-0.55208	0.006866	Bark
PO-15R*		0.042218	-1.29702	0.17008	Bark
PO-31	0.010936	0.010925	0.106396	0.021063	Pine
PO-51	0.018946	0.018955	-0.05172	0.028826	Pine
PO-52	0.009163	0.009212	-0.53178	0.009483	Leaves
PK-03*	0.004441	0.005399	-19.4719	0.054296	Moss
PK-04	0.005051	0.005106	-1.08623	0.004333	Grass
PK-13	0.007307	0.007332	-0.33667	0.009345	Moss
PK-14	0.007812	0.007822	-0.12859	0.00936	Grass
PK-31	0.007407	0.007363	0.597183	0.01136	Pine
PK-34*	0.005962	0.006073	-1.84124	0.028427	Grass
PK-51	0.007236	0.007260	-0.33075	0.010191	Pine
PK-52*	0.007148	0.007260	-1.5486	0.002015	Leaves
PK-85*	0.006627	0.006730	-1.54504	0.001721	Bark
V008-53-1	0.007421	0.007391	0.400429	0.07916	Pine

\* 235/238 ratio in unspiked sample.

\*\* 235/238 ratio from double-spiked sample after all corrections.

\*\*\* Relative percent difference  $100\% \times [(235/238)u - (235/238)ds] / \text{average}$ .

ORNL did replicate analyses from two separate filaments loaded from the same sample solution (Table 4). The standard deviations, absolute and relative, are at the  $1\sigma$  level and reflect the external precision (reproducibility) between the two sample loadings. Unfortunately, most  $^{235}\text{U}/^{238}\text{U}$  ratios were well removed from the natural value of 0.00725; the added accuracy provided by use of a double spike is not usually needed in such cases. In addition, some samples had insufficient uranium in them to give the desired count rate ( $> 1.0 \times 10^5$ ). Deciduous leaves and grasses, due to their seasonal nature, have never been the medium of choice in this application. Grasses in particular were deficient in uranium, while bark and moss gave the strongest signals in the mass spectrometer. Nonetheless, only three samples, two grasses and one deciduous leaves, gave relative external standard deviations that exceeded 1%, or, indeed, 0.5%. Samples that yielded count rates for  $^{238}\text{U}$  that exceeded  $10^5$  usually gave relative standard deviations well below 0.5%.

Table 4. ORNL Results from Environmental Samples

Sample	(235/238)	SD ( $1\sigma$ )	% RSD	Counts 238*	233/238	Type
PK-02	0.005497	0.000005	0.08	2.0e+07	0.338	Leaves
PO-02	0.1439	0.0006	0.42	1.9e+06	0.318	Leaves
PO-05	0.3022	0.0004	0.14	3.3e+07	0.160	Bark
PK-11	0.00716	0.00001	0.18	1.9e+06	0.268	Needles
PO-12	0.00993	0.00002	0.22	3.2e+07	0.121	Leaves
PK-15	0.006529	0.0000007	0.011	2.3e+07	0.254	Bark
PO-33	0.00837	0.00002	0.24	2.3e+07	0.336	Moss
PO-34	0.01408	0.00007	0.47	1.6e+05	0.180	Grass
PK-35	0.005706	0.00001	0.12	1.4e+07	0.131	Bark
PK-54	0.0071	0.00012	1.67	1.2e+06	0.072	Grass
PO-54	0.01279	0.00045	3.60	3.2e+05	0.234	Grass
PO-55	0.028796	0.000002	0.008	7.2e+06	0.291	Bark
PK-82	0.00996	0.00022	2.21	3.4e+06	0.238	Leaves
PK-83	0.00686	0.00001	0.14	2.1e+07	0.135	Moss
V008-50-1	0.00759	0.00003	0.42	1.5e+06	0.221	Needles
V008-52-1	0.007915	0.000007	0.09	1.6e+07	0.137	Needles
S009-03-5	0.00557	0.00001	0.26	1.7e+07	0.091	Swipe
S009-05-5	0.01251	0.00002	0.13	2.4e+07	0.009	Swipe
S010-05-5	0.05132	0.00002	0.04	3.0e+06	3.136	Swipe
S010-07-5	0.5050	0.0008	0.15	4.2e+06	3.530	Swipe

\* Sum of the count rate of  $^{238}\text{U}$  in count/sec from two filaments.

There is sufficient information in Table 4 to evaluate how well the double spike works on samples taken from the environment. The most important factor in such an evaluation is the external

relative standard deviation, which is listed for all samples in Table 4. Figures 1 and 2 are plots of percent relative external standard deviation versus  $^{235}\text{U}/^{238}\text{U}$  and total counts of  $^{238}\text{U}$  (sum collected from two filaments), respectively.

A plot of  $^{233}\text{U}/^{238}\text{U}$  versus relative external standard deviation gave results similar to that for  $^{235}\text{U}/^{238}\text{U}$ . There is no apparent correlation between relative external standard deviation and the two ratios, but there is good correlation with total counts. Any dependence of relative external standard deviation on the two ratios was masked by the larger effect of count rate. The three samples that gave relative standard deviations greater than 1% all had poor count rates; these results are poorer than would be suggested by the NIST U-950 results given in Table 2. This is almost certainly due to the fact that environmental samples are invariably dirtier than standards, which has deleterious effects on ionization efficiency and stability of the ion beam, and may also contribute isobaric interferences.

Some general statements can also be made by comparison of the ORNL and LANL data. As expected, samples collected from around Portsmouth (PO series) deviated more from natural than from those taken from around Paducah (PK); Paducah has enriched  $^{235}\text{U}$  only to the 3% level, while Portsmouth has gone to 90% and beyond. The Paducah samples, however, still deviate significantly from natural. Although replicate samples could not be provided, each laboratory received samples of different types taken from the same location. For example, the PK-8 samples were all taken eight kilometers from the Paducah gaseous diffusion plant, where bark, leaves, and moss were all collected. These samples are in no sense replicates; when pine needles taken from different limbs of the same tree yield uranium of different isotopic composition, it is unrealistic to expect agreement between results obtained from different types of vegetation. On the other hand, it is not unreasonable to expect such results to agree in a general sense, *i.e.*, all will show enrichment or depletion or be close to natural. This is basically what is found in our results. The Paducah samples comprise a better experimental test of the double spike method because the uranium in them is closer to natural. The three samples of the PK-0 series, for example, all contain depleted uranium (~0.5%). Those of the PK-5 series were all near natural. In essentially all cases, the ability to distinguish between slightly enriched and natural uranium was demonstrated; the only exceptions were when types of sample not recommended were involved. Grasses and deciduous leaves are poor media for the purposes of this experiment, while needles, bark, and moss all gave good results.

FIGURE 1. PLOT OF RELATIVE STANDARD DEVIATION vs. 235/238

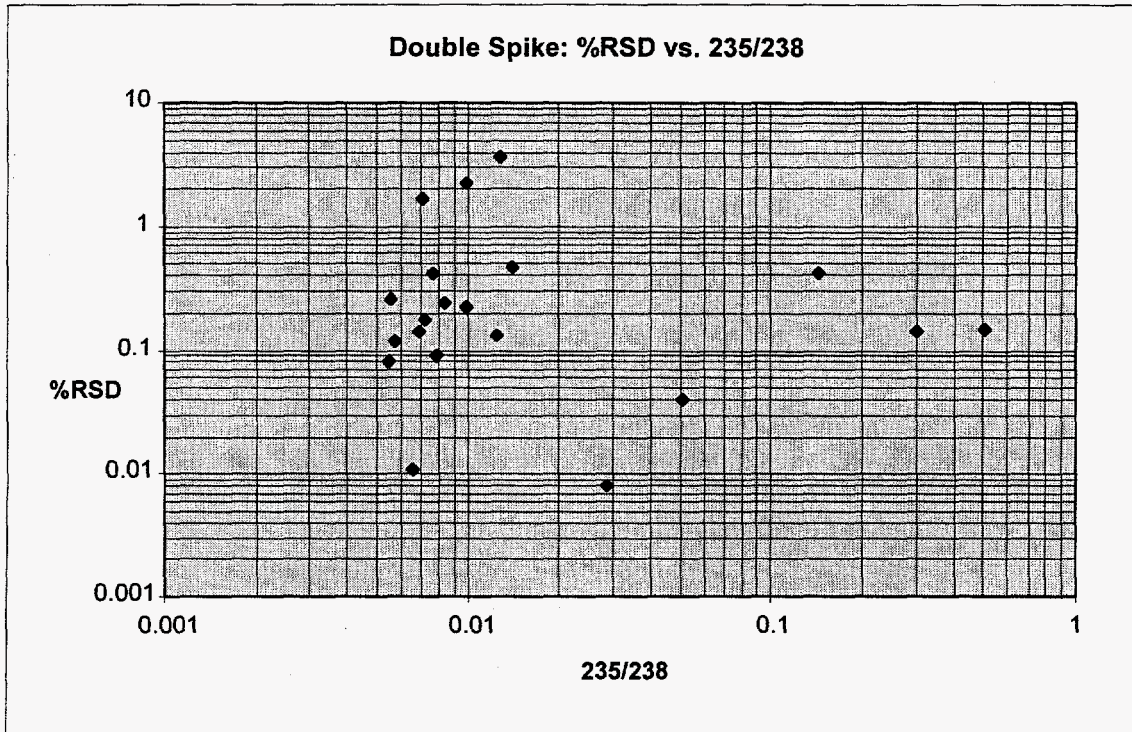
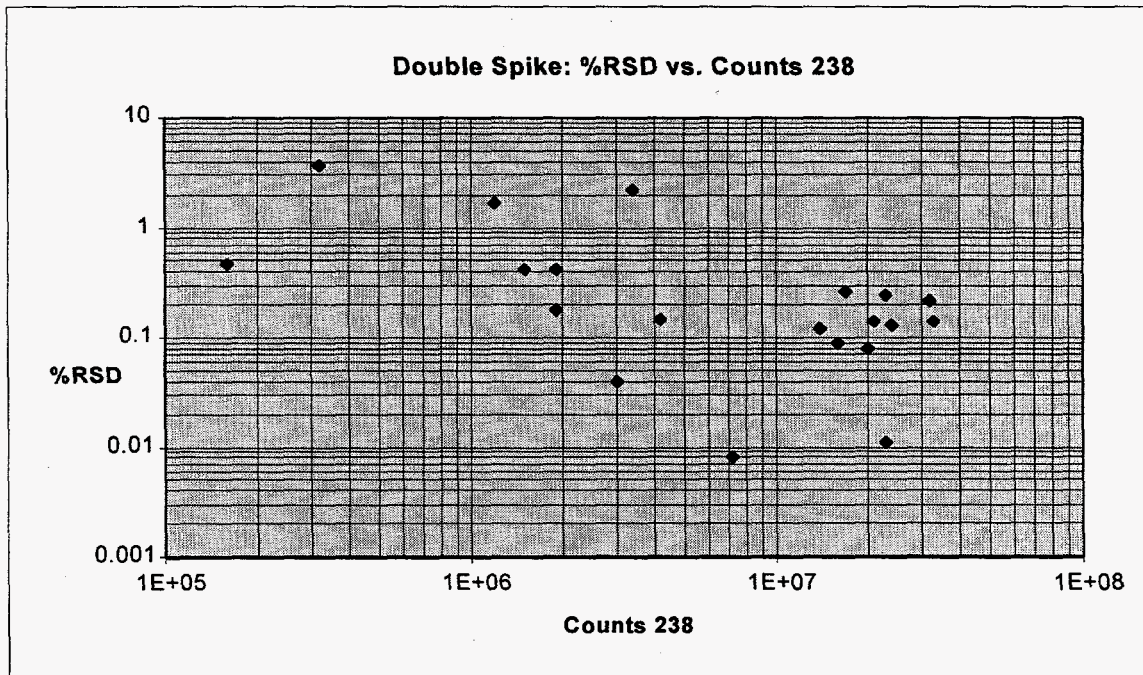


FIGURE 2. PLOT OF RELATIVE STANDARD DEVIATION vs. COUNTS 238



#### 4. CONCLUSIONS

Because of the nature of the environmental samples available for this experiment, replicate samples could not be used for evaluation of inter-laboratory agreement and to determine whether use of a double spike would reduce or eliminate errors due to instrumental bias factors. It was also not possible to evaluate accuracy because the isotopic composition of the samples was unknown. On the other hand, there are several observations that suggest that distinguishing 1% enriched uranium from natural should be readily achieved. The results given in Table 2 for NIST U-950 demonstrate this ability when standards are analyzed. The precision for most samples whose results are listed in Table 4 is well within the desired range. It is clear that choice of sample type plays an important role. Obtaining a count rate greater than  $10^5$  counts per second  $^{238}\text{U}$  is highly desirable, although not essential.



## 5. RECOMMENDATIONS

The next step in evaluating the power of the double spike is clearly to perform a multi-laboratory experiment using well-characterized samples. It is desirable, but not essential, that they be representative of real-world conditions. In this way, the full benefit of the technique should be established. It is important to evaluate the double spike's ability to reduce or eliminate calibration differences between laboratories. Performing an experiment on well-characterized samples in at least two laboratories should go a long way toward this end. The present experiment suggests that the following protocol be followed to eliminate bias between laboratories and to detect the smallest enrichment of  $^{235}\text{U}$  above natural:

1. A well-characterized spike must be used whose isotopic composition should be traceable to a certified isotopic standard.
2. The optimum sample-spike ratio is a function of the composition of the spike; the  $^{235}\text{U}$  abundance is of particular concern. This optimum value should be determined and the sample and spike mixed accordingly.
3. The isotopic composition of the sample must be determined so corrections can be applied to the 233 and 236 mass positions.
4. During analysis, it is highly desirable to obtain at least  $10^5$  counts per second of  $^{238}\text{U}$ .
5. For inter-laboratory comparison purposes, it is recommended that replicate filament loadings for each sample be analyzed. If the method is put into routine use, it will probably not be necessary to perform replicate analyses.

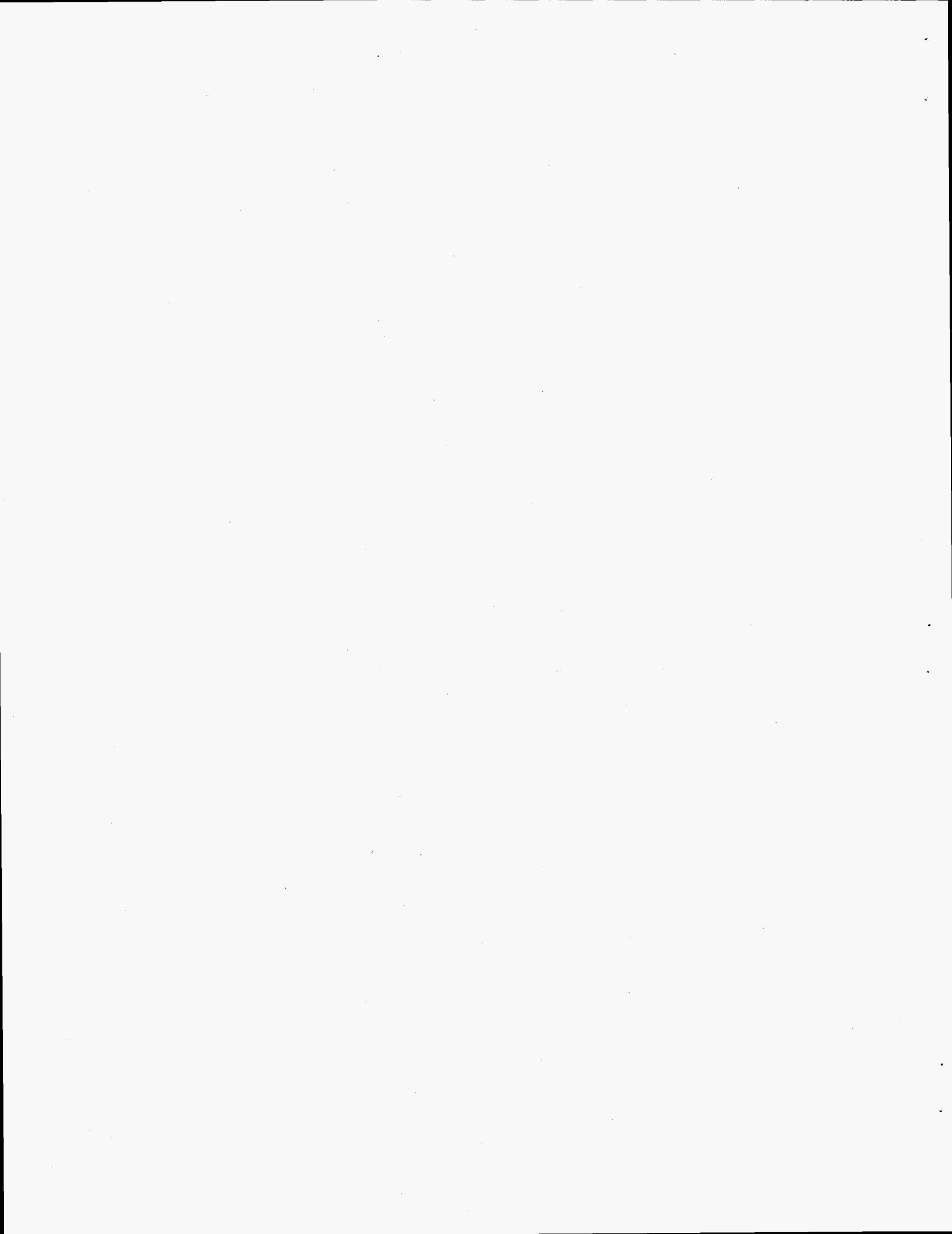
The International Atomic Energy Agency, at a meeting on the subject in Durango, Colorado, volunteered to provide well-characterized samples whose isotopic compositions are close to natural; with these samples a through evaluation can be carried out. We strongly support this experiment and urge its timely implementation.





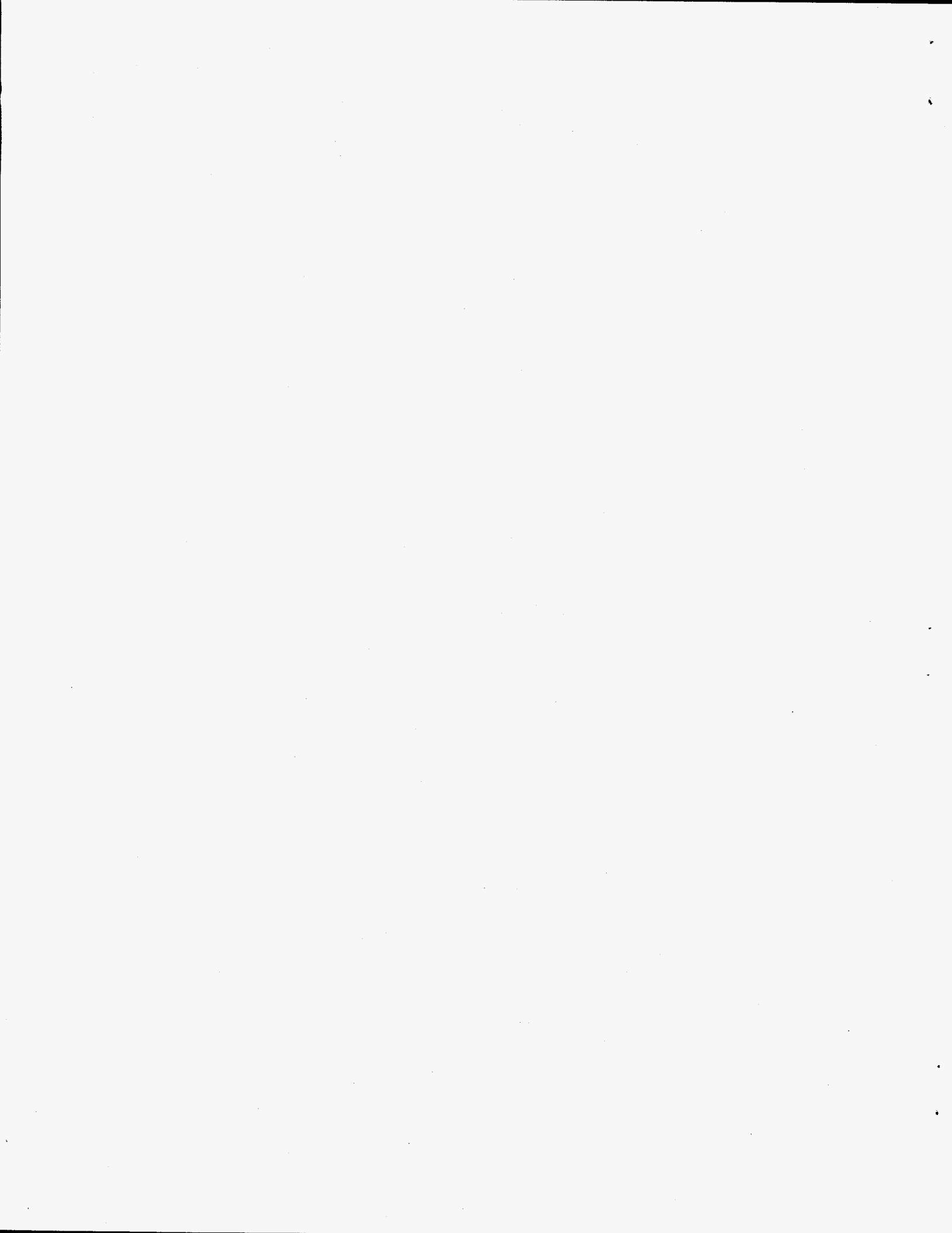
## 6. ACKNOWLEDGEMENTS

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