

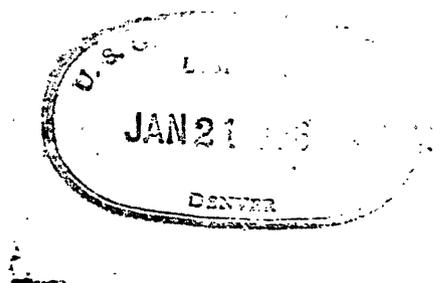
(200)  
R:295

UNITED STATES DEPARTMENT OF THE INTERIOR  
GEOLOGICAL SURVEY

Water and Stream-Sediment Sampling Techniques  
for Use in Uranium Exploration

By

Karen J. Wenrich-Verbeek



Open-File Report 76-77  
1976

This report is preliminary and has not been  
edited or reviewed for conformity with U.S.  
Geological Survey standards and nomenclature.

## CONTENTS

	<u>Page</u>
Abstract-----	1
Introduction-----	1
Water Sampling-----	2
Method of Filtration-----	5
Method of Analysis-----	7
Results of Filtration and Acidification-----	11
Variations in other Elements with Uranium Concentration-----	16
Stream-Sediment Sampling-----	18
Uranium Partitioning with Grain Size-----	19
Variations in other Elements with Uranium Concentration and Grain Size-----	26
Comparison of Water and Stream-Sediment Sampling-----	27
Conclusions-----	29
Acknowledgements-----	30
References Cited-----	30

## ILLUSTRATIONS

	<u>Page</u>
Figure 1.--Map showing locations of sampling sites-----	in pocket
2.--USGS Water Resources Division gaging station-----	3
3.--Conductivity meter-----	4
4.--Specific-ion meter-----	4
5.--Water sampler and disassembled filtration unit-----	6
6.--Use of water sampler in the field-----	6
7.--Assembled filtration unit-----	6
8.--Variation of uranium in samples filtered in the field with those unfiltered in the field-----	8
9.--Uranium variation in filtered unacidified with filtered acidified samples-----	9
10.--Uranium variation between unfiltered-unacidified and unfiltered-acidified samples-----	10
11.--Variation of uranium concentration with length of time between sample collection and analysis-----	14
12.--Variation between nuclepore with surfactant and without and millipore filters-----	17
13A--Uranium concentration versus grain size-----	20
13B--Uranium concentration versus grain size-----	21
13C--Uranium concentration versus grain size-----	22
13D--Uranium concentration versus grain size-----	23
14.--Uranium concentration in water versus uranium concentration in corresponding stream sediments-----	28

## TABLES

	<u>Page</u>
Table 1.--List of uranium concentrations for dissolved and suspended fractions-----	12
2.--Uranium concentrations for stream sediments-----	24

# WATER AND STREAM-SEDIMENT SAMPLING TECHNIQUES FOR USE IN URANIUM EXPLORATION<sup>1</sup>

By Karen J. Wenrich-Verbeek

## Abstract

Methods of sampling water and stream sediments for uranium were established in this study. Water samples should be taken using a US DH-48 water sampler across the stream channel and should be filtered and acidified in situ. Stream sediments should be taken as a composite sample up and across the axis of the channel. Only sediment fractions less than 90  $\mu\text{m}$  (170 mesh) should be analyzed for uranium. The elements As, Ca, Al, B, Mg, K, and Na exhibit a positive correlation with uranium in surface waters, while a much larger suite of elements exhibit a positive correlation with uranium in stream sediments: K, Mn, Mg, Ti, Ca, Al, Fe, Pb, Cr, Y, Zr, Li, Zn, Th, and As. Analyses have revealed that anomalies detected in either the dissolved or suspended fractions of water, or the stream sediments, are frequently not reflected in the other two; hence, all three should be sampled and analyzed.

## Introduction

The distribution of uranium in surface waters is being studied for use as a technique for exploration because of the urgent need to locate additional uranium deposits, notably in the subsurface. Surface waters carry dissolved elements from both surface rocks and subsurface rocks, and, although these waters do not provide as good an evaluation of subsurface terrane as ground-water wells, this sampling is definitely a cheaper, faster, and more far-reaching method of exploration.

---

<sup>1</sup>Based on a talk presented December 10, 1975, at the U.S. Geological Survey's 1975 Uranium and Thorium Research and Resources Conference, Golden, Colorado, and a poster session at the Geological Society of America's annual meeting, November 1975.

Before the use of uranium in surface waters and stream sediments can be tested as a tool in uranium exploration, methods of sampling need to be established. To achieve this, 16 sampling sites were chosen within Colorado, New Mexico, and Arizona (fig. 1-in pocket). These streams drain a broad variety of geologic terranes and represent various major drainage basins. Some of them have known uranium reserves upstream.

Sites were chosen at U.S. Geological Survey gaging stations along each stream. One benefit of this procedure was that the best sampling date could be selected to minimize effects of excess runoff that might dilute the ground-water contribution to the stream (the sought-after tracer of buried deposits), and to measure exact discharge. A water level reading was recorded from each gaging station (fig. 2) at the time of sampling; this information was used to calculate the exact discharge. An additional benefit is the availability in the USGS records and the Storet file, of other water parameters, occasionally including numerous trace elements, monitored at these gaging stations on a regular basis. Data from samples taken at each site were studied for effects of filtration, acidification, and location within the stream channel.

Along with discharge other parameters measured in situ were water temperature, conductivity (fig. 3), and pH and Eh (fig. 4). Stream sediment samples were also collected with each water sample. These were studied for elemental concentration variations within different size fractions and between different geomorphic locations within the stream channel.

#### Water Sampling

Water samples were taken using a US DH-48 water sampler (fig. 5) designed to maximize homogeneity of suspended material as well as water

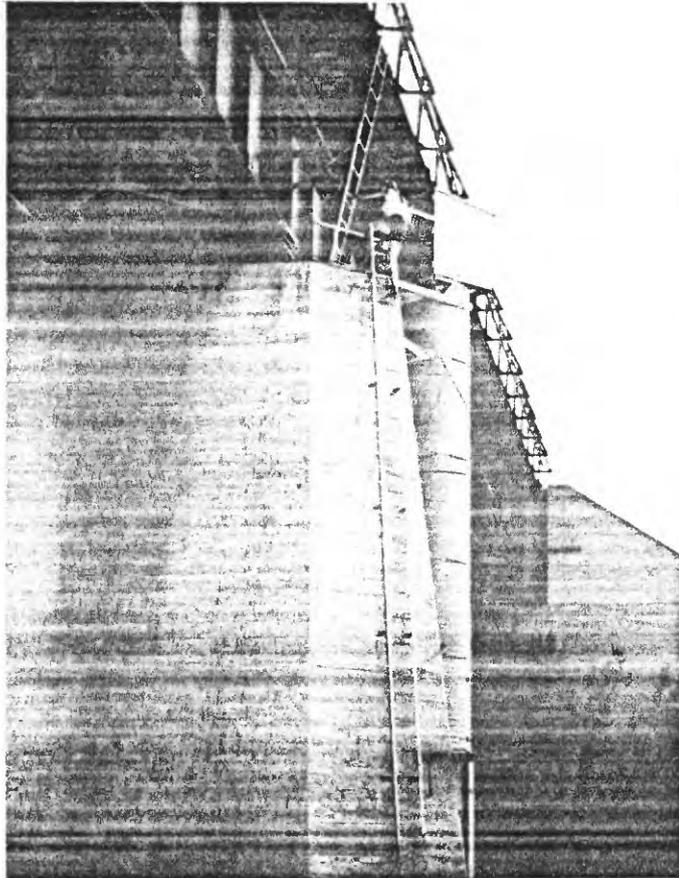


Figure 2.--USGS Water Resources Division gaging stations are being used for discharge measurements at each sample site--a parameter useful in evaluating the uranium content in streams. Rio Puerco, New Mexico.

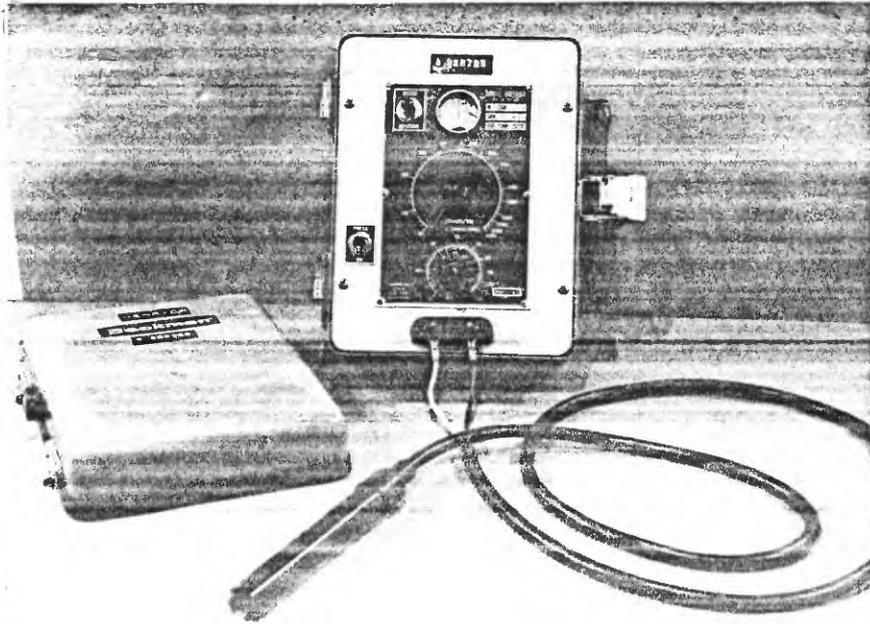


Figure 3.--Beckman conductivity meter permits readings to  $\pm 5\%$  in less than one minute.

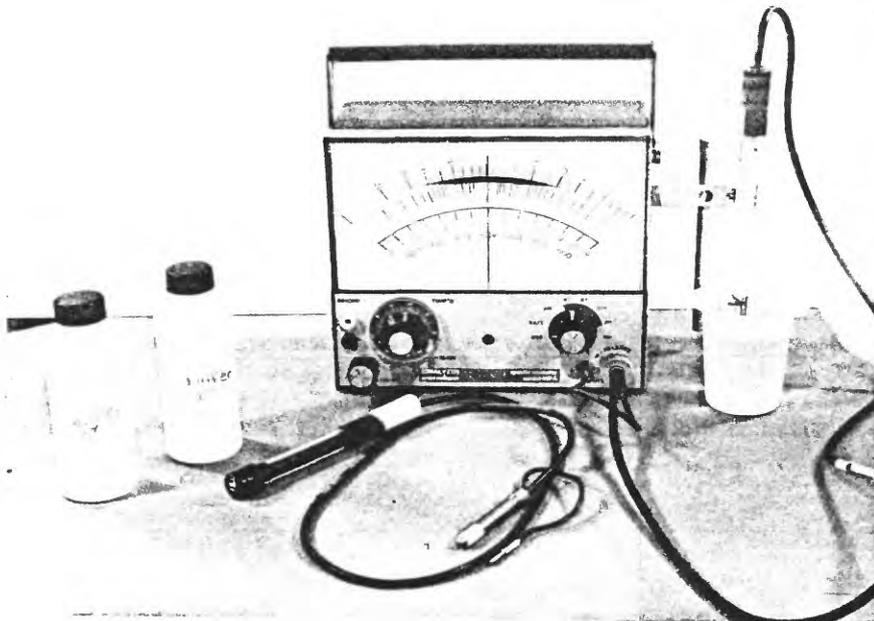


Figure 4.--Orion specific-ion meter used for pH (electrode attached to meter) and Eh (electrode in foreground) field measurements in water sampling for uranium.

(Guy and Norman, 1970). Depth-integrated samples were acquired by lowering the sampler to the channel bottom at various intervals (see Guy and Norman, 1970, p. 26-30, for discussion of interval selection) as the geologist waded across the stream (fig. 6). The water collected in the flint-glass sampler bottle was then transferred to the polyethylene collection bottle that had been rinsed with reagent grade nitric acid, diluted to a pH of approximately 2. Rinsing causes some available sites on the container surface to be filled with hydrogen ions, minimizing later loss by uranium ions into these areas.

Analyses of individual samples taken along the bank and midstream of the Jemez River using the sampler were compared to composite samples, which comprised eight separate dips across the channel. There was no apparent difference between the uranium content of the three samples (0.27  $\mu\text{g}/\ell$  = ppb - composite; 0.26  $\mu\text{g}/\ell$  - midstream; 0.22  $\mu\text{g}/\ell$  - bank). At this location, the Jemez River is a small, very clear, rapidly flowing stream, even along the bank, with a channel width of five meters. Thus, sampling solely by the bank for large turbid streams may not be wise, but such a procedure may be assumed, with minimum inhomogeneity, for similar mountain streams.

#### Method of Filtration

Samples were filtered in the field using the filtration unit shown in figure 7. Passage of the water through the filter was accelerated by use of a small nitrogen tank. Even for the most turbid water samples, the filtration time for a 1 liter sample is less than 15 minutes.

A sample of the sediment-laden water of the Rio Puerco was allowed to settle for two hours and then filtered. This was done in an attempt to determine whether pre-settling could be adopted in order to accelerate

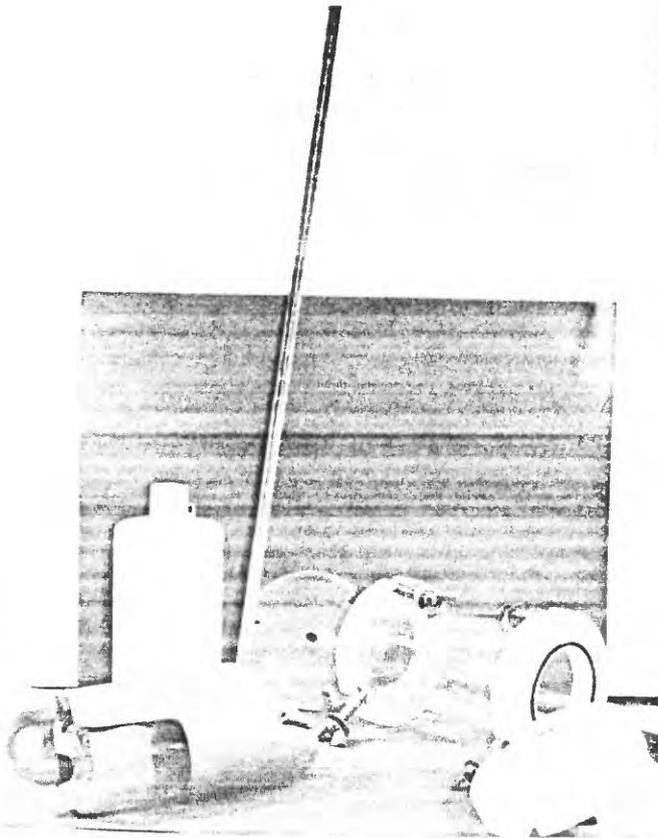


Figure 5.--Water sampler and disassembled filtration unit (millipore filter mounted on the base).

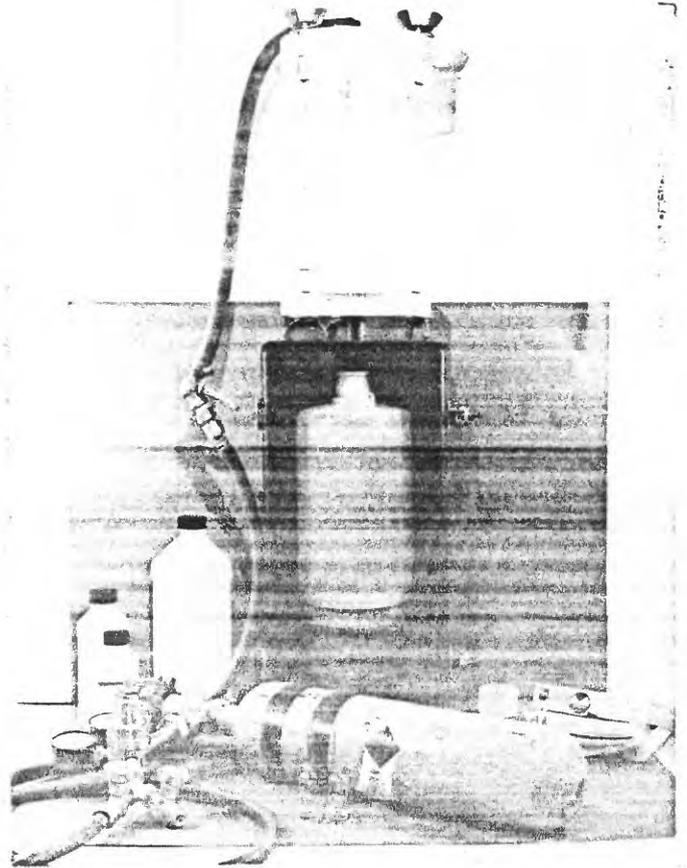


Figure 7.--The filtration unit, used with a small, lightweight nitrogen tank facilitates rapid filtration through 0.45  $\mu$ m millipore filters. Small glass ampules in the foreground, prepared in the laboratory, contain sufficient nitric acid to acidify each water sample to a pH less than 1.

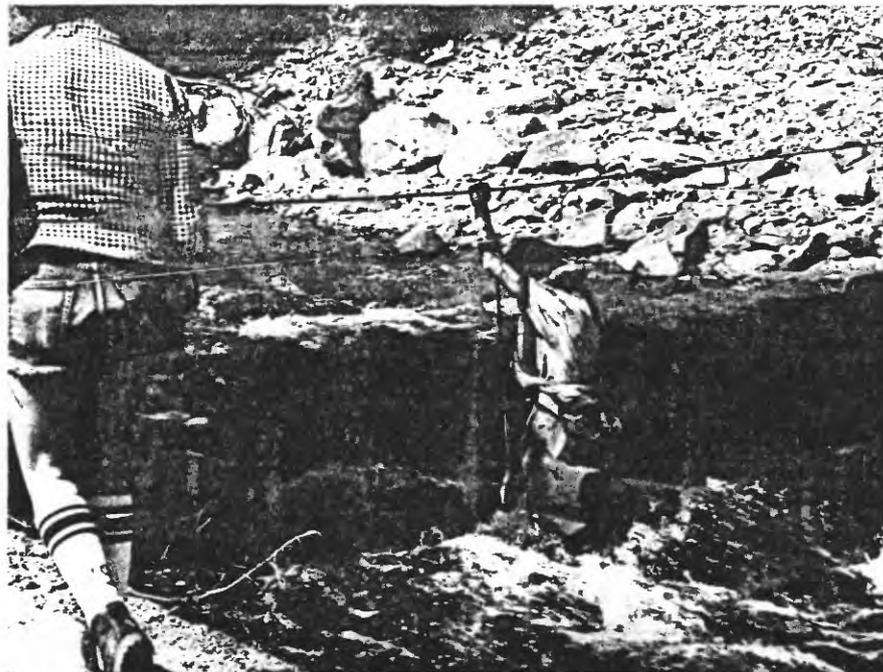


Figure 6.--Use of a US DH-48 water sampler in the field permits a more complete sampling of the entire channel. Mineral Creek, Col.

filtration of quantities over 300 ml of murky waters that tend to clog the filter. The answer to this was definitely "No": The sample apparently gained uranium ( $8 \mu\text{g}/\ell$  for the settled sample compared to  $5 \mu\text{g}/\ell$  for promptly filtered samples). On the other hand, if the Rio Puerco samples are allowed to stand unfiltered for several weeks before analysis, some of the uranium from solution goes back into the suspended material; the unfiltered samples from this site averaged about  $6 \mu\text{g}/\ell$ .

Millipore filters with a pore diameter of  $0.45 \mu\text{m}$  were used for all samples. In addition, some samples were also filtered through two types of nuclepore filters: (1) with surfactant ( $0.40 \mu\text{m}$ ), and (2) without surfactant ( $0.45 \mu\text{m}$ ). This was done to water samples analyzed for both uranium and twenty trace and major elements.

#### Method of Analysis

Samples were analyzed by both the U.S. Geological Survey (USGS), Denver, Colorado, and the Oak Ridge Gaseous Diffusion Laboratory (ORL), Oak Ridge, Tennessee. Both laboratories analyzed the samples for uranium by use of direct and extraction fluorimetry (Barker and others, 1965) with limits of detection down to  $0.01 \mu\text{g}/\ell$  (USGS) and  $0.03 \mu\text{g}/\ell$  (ORL). The agreement between the analytical results is excellent (figs. 8-10).

Although the standard analytical method of fluorimetry permit determination of uranium to sufficiently low concentrations, it requires 1-litre samples that are cumbersome to handle and transport in the quantities involved in a large-scale uranium exploration program. This method of collection also presents problems of container adsorption and loss of uranium on transfer. These problems can be eliminated by a newer analytical technique for uranium, the fission-track technique. This has been adapted to uranium exploration in water, using a  $25 \mu\ell$  drop of water, by G. M. Reimer (written

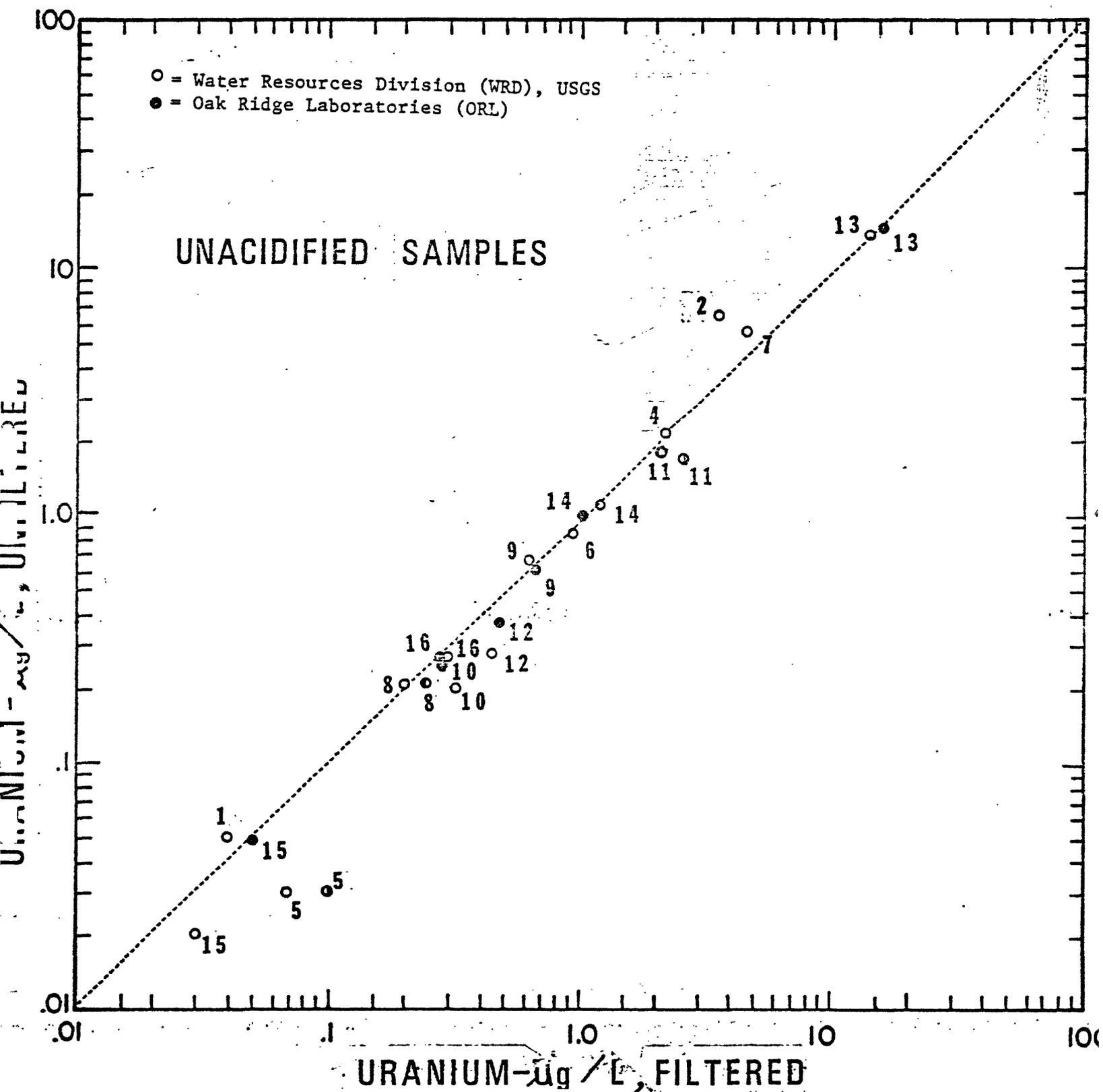


Figure 8.—Variation of uranium in samples filtered in the field with those unfiltered in the field but later filtered in the laboratory. Line represents points at which there is no difference in the two sample types. A comparison of results by ORL and WRD, USGS, on the same samples (number indicates sample site) gives an estimate of the precision of the fluorimetric determinations.

JR...U... μg, L JN...SIL...IEC

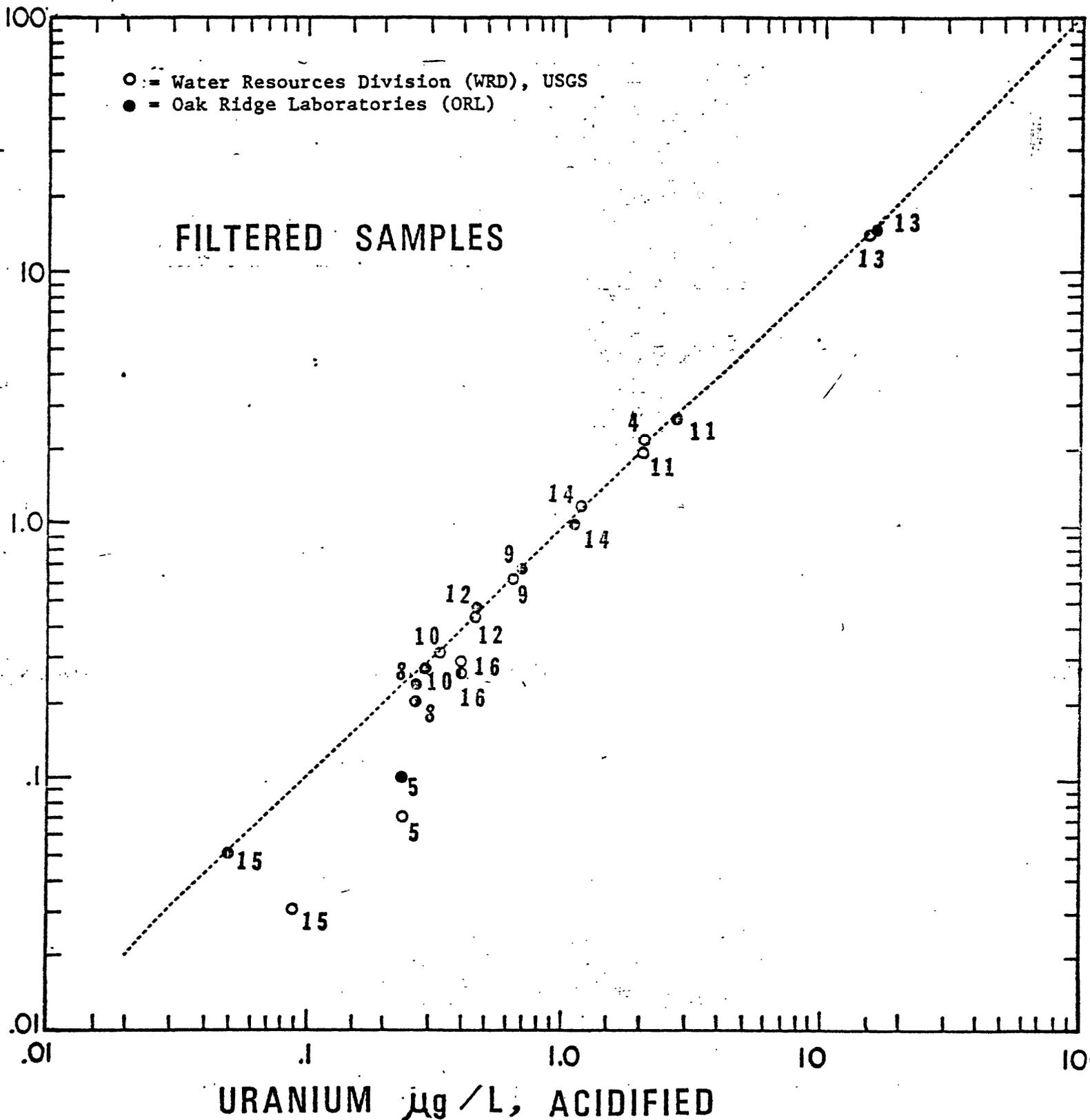


Figure 9.--Uranium variation in filtered unacidified with filtered acidified samples. Line represents points at which there is no difference in the two sample types. A comparison of results by ORL and WRD, USGS, on the same samples (number indicates sample site) gives an estimate of the precision of the fluorimetric determinations.

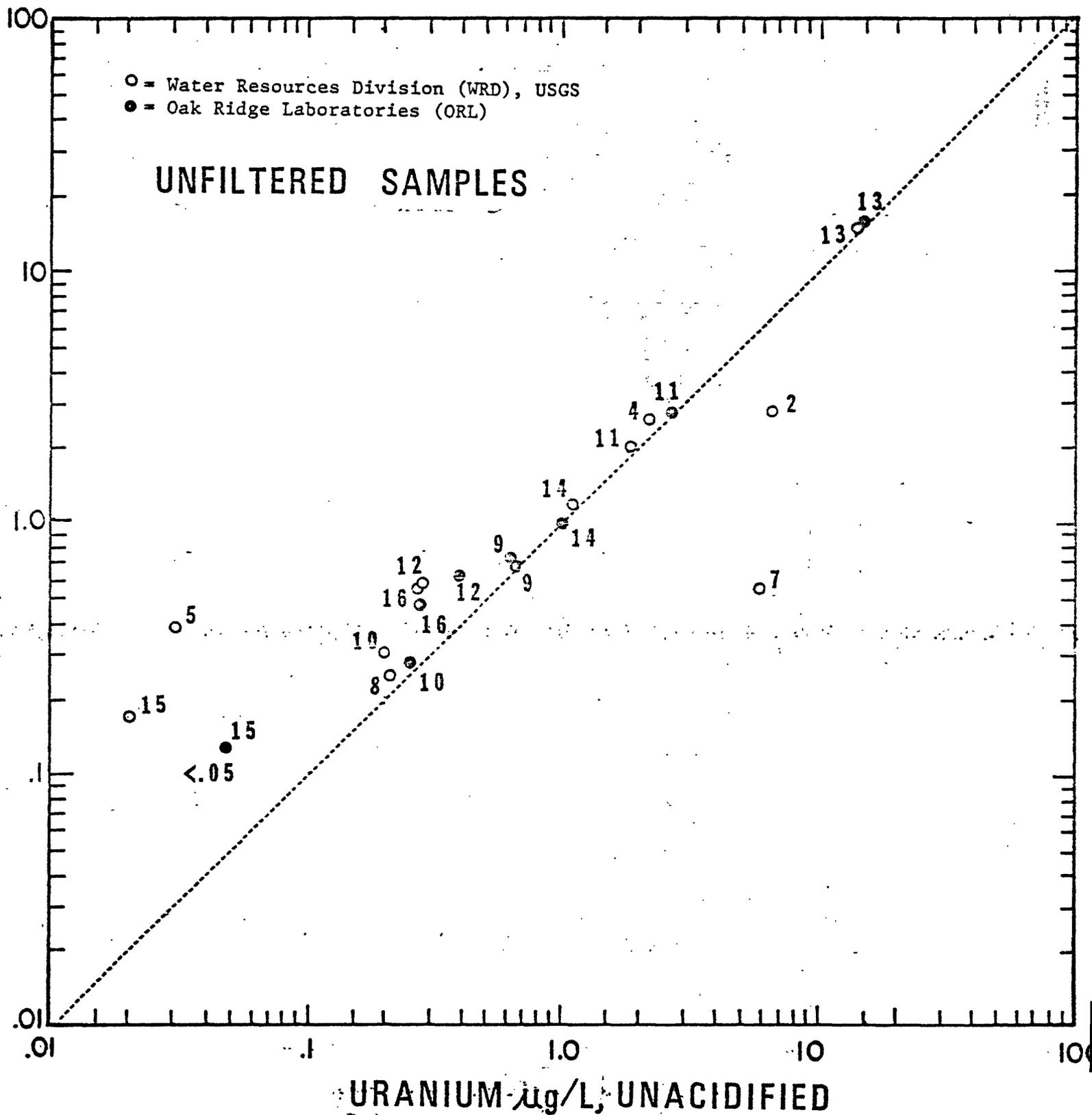


Figure 10.--Uranium variation between unfiltered-unacidified and unfiltered-acidified samples. Line represents points at which there is no difference in the two sample types. A comparison of results by ORL and WRD, USGS, on the same samples (number indicates sample site) gives an estimate of the precision of the fluorimetric determinations.

communication). Fission-track determinations have been made on some of the same samples as determined by fluorimetry, with good agreement in the results as shown in table 1.

#### Results of Filtration and Acidification

Four samples taken at each site represent combinations of filtered, unfiltered, acidified (using ultrex nitric acid and acidifying to a pH less than 1), and unacidified. The unfiltered samples were later filtered in the laboratory 3 to 8 weeks later and analyzed simultaneously with the field-filtered samples (fig. 7).

Two values of uranium were determined by separate laboratories for each sample and are plotted on figures 8, 9, and 10 which show the precision of the analyses between the two laboratories as well as the effects of different sample treatment procedures. Although the uranium content varies from 0.02 to 15  $\mu\text{g}/\ell$ , a range found in most natural waters, there is little variation in concentrations greater than 0.6  $\mu\text{g}/\ell$  from the "line of equivalence" ( $45^\circ$  slope from the origin). There appears to be an almost insignificant difference in uranium concentrations above 0.6  $\mu\text{g}/\ell$  between samples filtered through 0.45  $\mu\text{m}$  millipore filters in the field (fig. 8) as compared to those filtered later in the laboratory. Figure 8 shows values slightly higher for the filtered-unacidified samples than for unfiltered-unacidified samples. For most values above 0.6  $\mu\text{g}/\ell$  these differences are no more than twice the error in analytical precision with the exception of samples 2 and 7. These two samples, especially sample 7, were considerably more turbid than the others. Figure 10 shows an even greater deviation from the "line of equivalence" for these two samples when unfiltered, emphasizing the problems involved when turbid samples are allowed to stand unfiltered. The slightly lower values in the laboratory filtered samples can be attributed to the adsorption of some uranium onto the particulate material during the

Table 1.--List of uranium concentrations for dissolved and suspended fractions of: (1) field-unfiltered samples for comparison between acidified and unacidified samples, and (2) field-filtered samples, acidified and unacidified

[All analyses were done by fluorimetry at Oak Ridge Gaseous Diffusion Laboratories except those in parentheses (total only), which were done by fission track\* and those marked by\*\* done by Water Resources Division, USGS. \*Fission-track analyses were done on samples taken from the same sample site with the fluorimetry samples. Technique used was that developed by G. M. Reimer. (Written communication, 1975).]

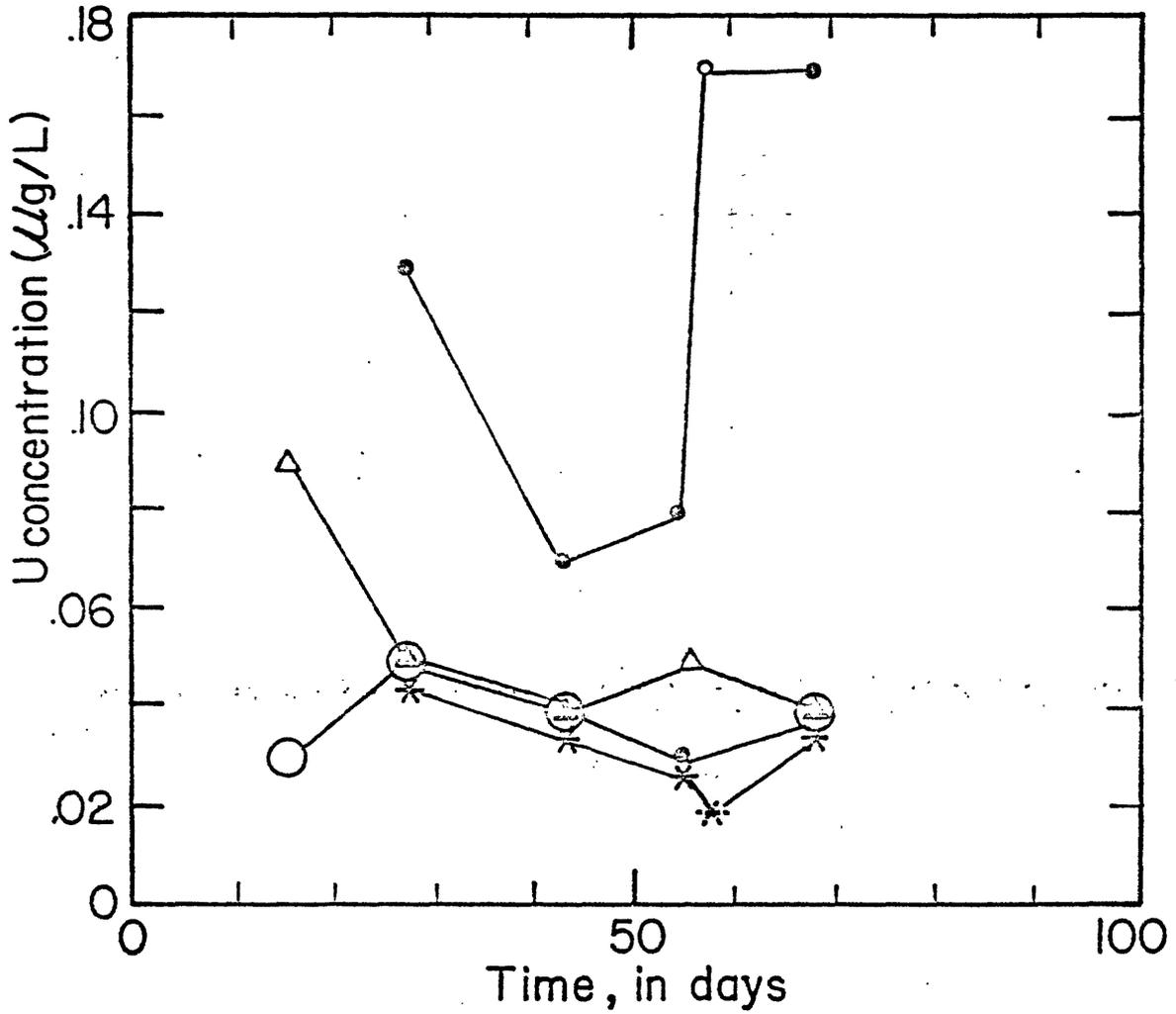
Sample Site	Dissolved + Suspended = Total (µg/ℓ)		Filtered-Unacidified	Filtered-Acidified	Comments
	Unfiltered-Unacidified	Unfiltered-Acidified			
1	0.05	---	0.04**	---	
2	6.5 **	2.8**	3.6**	---	
3	0.68**	---	---	---	
4	2.64 + 0.48 = 3.12	---	2.2	2.1	
5	0.17 + 0.12 = 0.29	0.16 = <0.08 = 0.16	0.7	0.24**	
6	1.24 + 0.64 = 1.88	---	---	---	
7	6.07 + 255 = 261	4.90 + 181 = 186	---	---	
8	0.26 + <0.08 = 0.26	0.29 + <0.08 = 0.29	0.20	0.27**	Midstream Bank
9	0.22	0.74 + 0.08 + 0.82	0.63	0.65	
10	0.25 + 0.50 = 0.75 =(0.75)*	0.28 + <0.08 = 0.28	0.32	0.33	
11	2.7 + 0.41 = 3.11	2.8 + 0.54 = 3.34	2.67	2.1**	
12	0.38 + 0.50 = 0.88	0.62 + 0.25 = 0.87 =(0.55)	0.44	0.46	
13	14.2 + <0.08 = 14.2 (27.0)	15.9 + 0.30 = 16.2	15.84**	16.0**	
14	1.0 + 0.18 = 1.18 (2.2)	1.0 + 0.15 = 1.15 (1.9)	1.2	1.2	Replica, Unacid.
15	<0.05 + 0.17 = 0.17 <0.05 + 0.13 = 0.13 <0.05	0.13 + <0.04 = 0.13 0.07 + 0.12 = 0.19 0.08 + 0.08 = 0.16	0.03	0.09	After 27 days After 43 days After 55 days After 68 days
16	<0.05 + 0.31 = <0.36 <0.05 + 0.19 = <0.24 (0.3)	0.17 + 0.08 = 0.25 0.48 + 0.03 = 0.51 (0.45)	0.29	0.40	

3 to 8 weeks of storage prior to filtration and to the consequent loss of particulate matter upon filtration.

Acidification of filtered samples (fig. 9) shows only a slight effect on the uranium content, notably samples with values less than 0.5  $\mu\text{g}/\ell$ , which show a slightly higher concentration than unacidified samples. This is probably a result of the large hydrogen ion concentration, which results in hydrogen ions occupying available exchange sites in the container walls, thus reducing the available sites for uranium.

Acidification of unfiltered samples should be avoided. The acidified-unfiltered samples show a significant increase in uranium content (fig. 10)-- a result of the lower pH allowing dissolution of a substantial amount of the uranium from the suspended material which is later filtered out in the laboratory. This dissolution of elements from the suspended material is even more pronounced for radium, which in some unfiltered-acidified samples increases as much as one order of magnitude over the corresponding unfiltered-unacidified sample. The result of the dissolution is even more apparent in figure 11, which shows the variation of each of the four treated samples with time for a sample of low uranium concentration. On the other hand, the unfiltered-unacidified samples show lower uranium concentrations than do the two sets of filtered samples (fig. 11), which can be attributed to the adsorption of a small amount of uranium onto the suspended material, which is then lost from the sample upon filtration prior to analysis. Table 1 shows the dissolution of uranium from the suspended material of unfiltered-unacidified samples when unacidified and acidified samples are compared for dissolved and suspended fractions.

Samples unfiltered in the field and later filtered in the laboratory tend to either gain or lose uranium depending on whether or not they were



- filtered, unacidified
- △ filtered, acidified
- \* unfiltered<sup>1</sup>, unacidified
- unfiltered<sup>1</sup>, acidified
- open symbols=sample analyzed by WRD, USGS
- closed symbols=samples analyzed by Oak Ridge Laboratories
- <sup>1</sup>filtered later in the laboratory

Figure 11.--Variation of U concentration with length of time between sample collection and analysis for Mineral Creek (Site 15).

acidified. If unfiltered-acidified samples are used, most of the uranium, both dissolved and suspended, will end up in the filtrate, although this is not always the case depending on the nature of the suspended material. Due to these inconsistencies, for most uranium exploration a total leachate is not desired. Following such a procedure would result in the uranium content being totally dependent on the quantity of suspended sediment in the stream. Sediment content is positively related to the surface runoff. A heavy rain upstream could thus result in more inconsistent changes in the uranium concentration of unfiltered-acidified samples than would filtered-acidified samples.

Although filtered-acidified, filtered-unacidified, and unfiltered-unacidified samples (fig. 9) exhibit similar analytical results above about 0.5  $\mu\text{g}/\ell$ , at lower uranium concentrations filtered-unacidified and unfiltered-unacidified samples tend to lose some of their uranium to the polyethylene container and to the suspended material.

Thus, it is recommended that filtered-acidified samples be taken, especially for lower values. Because the Geological Survey of Canada has uncovered an anomaly at the 1.0  $\mu\text{g}/\ell$  uranium level in the Beaver Lodge area, Saskatchewan (Willy Dyck, 1975, oral communication), values below 0.5  $\mu\text{g}/\ell$  are important and need to be considered. If a stream is extremely clear, particularly in areas where helicopters are necessary and time is critical, it might be preferable not to filter. In those circumstances, the entire study area must be treated the same, and the assumption is then made that a proportional quantity of suspended material is carried in each stream. This is not usually the case and unless the suspended material is almost negligible it will likely result either in some insignificant anomalous values or in some that are overlooked.

Increased uranium concentration in the suspended fraction (residue upon filtration in the field) shows no correlation with that in the dissolved fraction (table 1). This is to be expected, because the uranium concentration in the suspended fraction is dependent on the mineral species present as well as the clay and organic content. For this reason if the suspended fraction is not also analyzed, anomalous areas may be missed under some geochemical conditions, such as inadequate pH conditions or insufficient concentrations of anions such as sulfate and carbonate, to allow the uranium to go into solution.

Uranium contents are similar for millipore and nuclepore filters with the exception that filtration through nuclepore with surfactant produces consistently lower uranium results for nuclepore filters without surfactant (fig. 12). This suggests that either the surfactant adsorbs a minor amount of uranium ions or the slightly smaller pore size removed material between 0.40  $\mu\text{m}$  and 0.45  $\mu\text{m}$  that contains a significant amount of uranium. Though uranium values are similar for both nuclepore without surfactant and millipore, more radium is lost through millipore paper than through nuclepore without surfactant. Some of the trace elements exhibit no differences between millipore and nuclepore, whereas others do. Further study of these trace element trends is planned.

#### Variations in other Elements with Uranium Concentration

There are fewer elements which correlate with uranium in water than in stream sediments; this is due partly to the lower concentration of most elements in water, frequently below the detection limit, and partly to the dependence of their solubility on other conditions, such as the presence of anions needed to form soluble complexes. Elements which increase with increasing uranium content in surface water are As, Ca, Al, B,

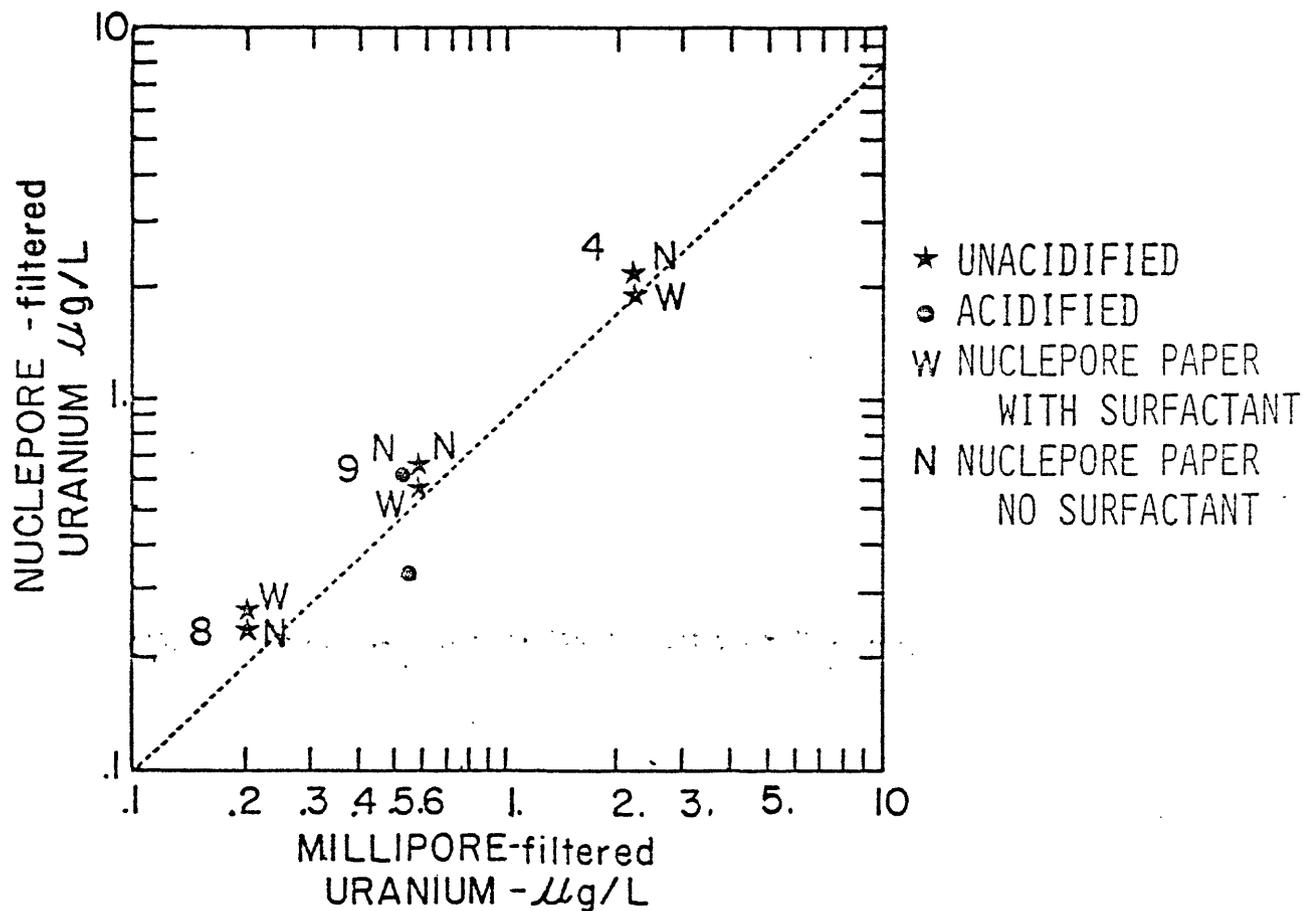


Figure 12.--Variation between nuclepore with surfactant and without and millipore filter papers. Numbers indicate sample site and the line represents points at which there is no difference in uranium concentration between samples filtered through millipore and nuclepore filters.

Mg, K, and Na. Three metallic ions, Zn, Cu, and Mn, actually appear to have a low negative correlation with uranium in water.

Most of the trace elements studied show less loss into the container and less gain from the suspended material if the sample is filtered and acidified as compared to the other three treatments studied. Most of the element loss or gain in unfiltered samples appears to occur before the 40th day; after that the fluctuations in element concentrations in solution begin to level off.

Although only seven cations (mentioned above) in water exhibit a strong positive correlation with uranium, a number of anions exist that should be determined with uranium and these cations. Those that should be included are sulfate, carbonate and phosphate; the latter can be used as an indicator of the uranium concentration contributed by fertilizer contamination.

#### Stream-Sediment Sampling

Stream-sediment samples were taken with water samples. Multiple samples were taken at most sites; generally they represented composites of 15 or more grab-samples from the stream bed, across the channel, and occasionally from specific locations within a meander.

The samples were placed in polyethylene bags, so as to avoid losing the very fine clay fraction, and dried at less than 110°F within 2 weeks of collection. The samples were separated, in stainless steel sieves, into the following seven size fractions:

<u>Group</u>	<u>Sieve mesh size</u>	<u>Grain size in micrometres</u>
1.	> 60	> 250 $\mu\text{m}$
2	60 - 100	149-250 $\mu\text{m}$
3	100 - 140	105-149 $\mu\text{m}$
4	140 - 200	74-105 $\mu\text{m}$
5	200 - 230	63-74 $\mu\text{m}$
<del>6</del>	<del>230 - 325</del>	<del>44-63 <math>\mu\text{m}</math></del>
7	< 325	< 44 $\mu\text{m}$

Each size fraction was then analyzed for uranium by delayed neutrons and for about 40 major and trace elements by atomic absorption and quantitative spectrographic analyses, to determine which grain size interval is the most suitable for detecting anomalous concentrations of uranium and correlating elements.

#### Uranium Partitioning with Grain Size

Samples from all 16 sites sampled for stream sediments exhibit a preference of uranium for sizes less than 90  $\mu\text{m}$  (figs. 13A-D). The uranium concentration, in most cases, appears to be least for the 100 to 200  $\mu\text{m}$  fractions, and then increases slightly in the coarser fractions. In general, the variation between samples taken at the same site is minor as reflected in the similar trends of uranium concentration versus grain size trends (figs. 13A-D).

The uranium concentrations in these sediment samples varies from less than 0.5 ppm to 27 ppm (finest fraction of Rock Creek). The uranium concentration increases significantly from the 250  $\mu\text{m}$  (60 mesh) size fraction to the 44  $\mu\text{m}$  (325 mesh) fraction in each sample. Deviations between replicate samples is greater for samples of high uranium concentration (over 10 ppm) than for those of lower concentrations, emphasizing the difficulty involved in taking a representative sample of stream sediments when uranium is concentrated either in, or adsorbed on, certain mineral or organic phases.

If anomalous concentrations of uranium are not to be overlooked, the sample must not be diluted with the coarse, low-uranium fraction. For instance, sample 16 (Rock Creek) with the greatest uranium concentration shows the following uranium values (see also table 2) and weights for each split:

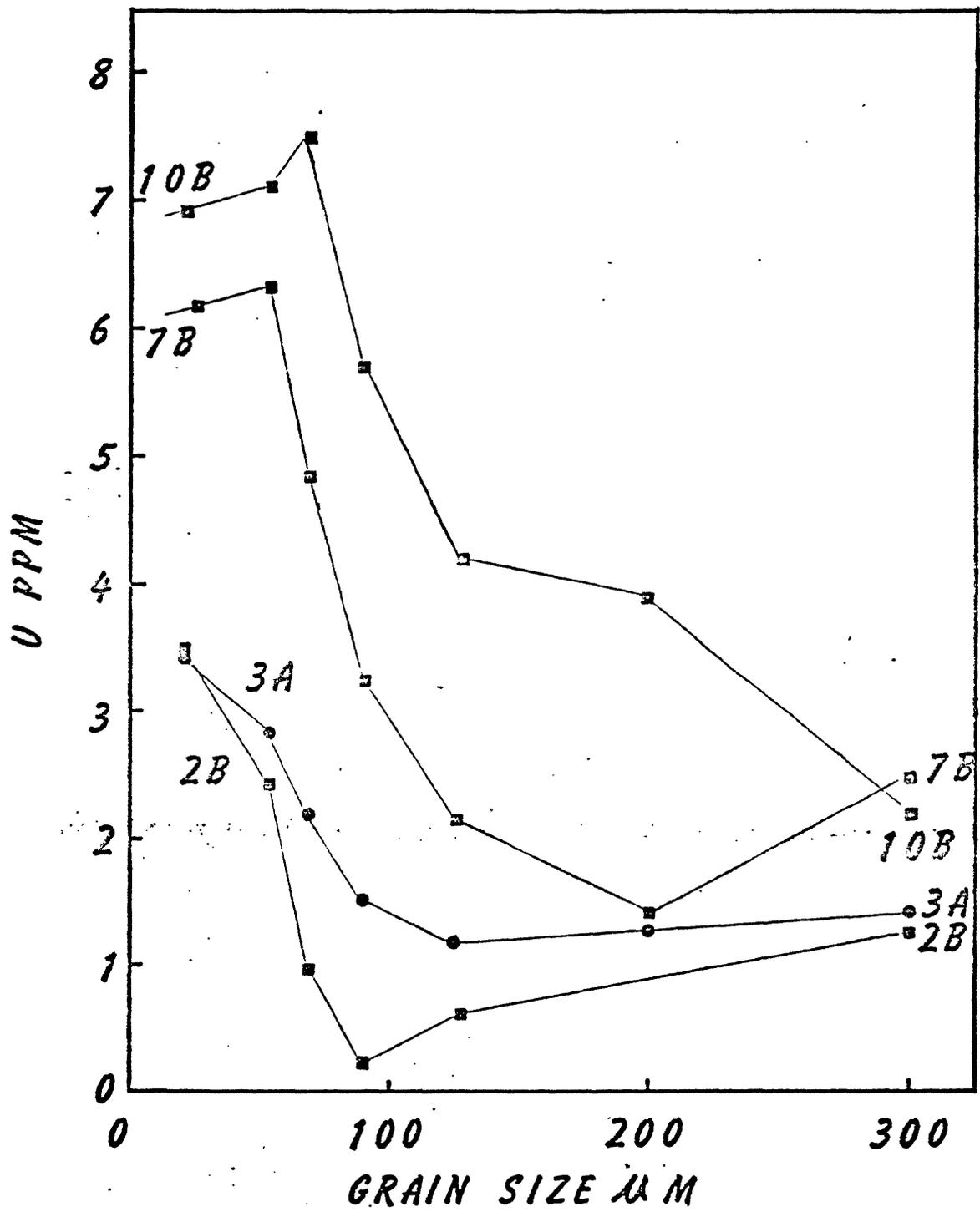


Figure 13A. Uranium concentration versus grain size in stream sediments.

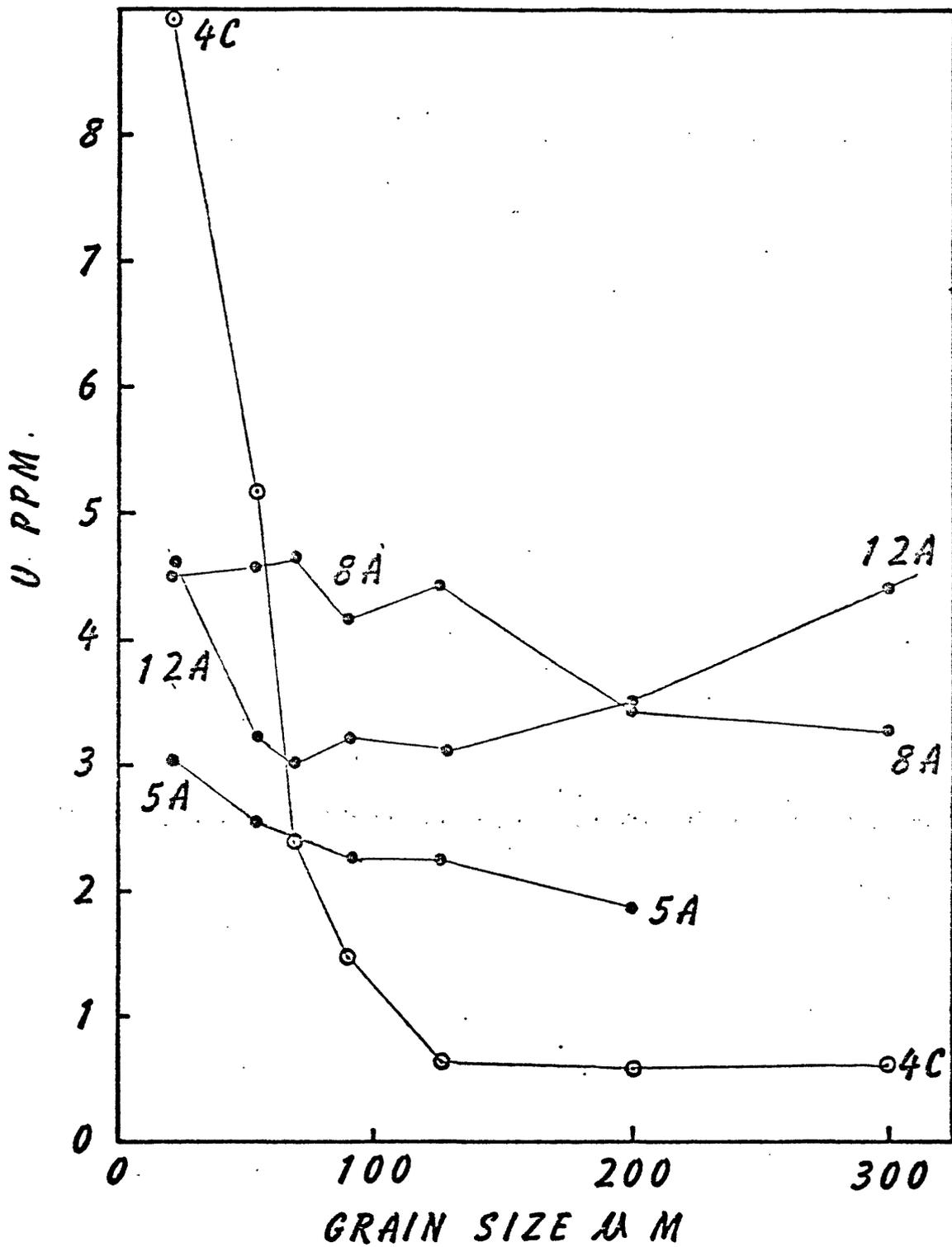


Figure 13B. Uranium concentration versus grain size in stream sediments.

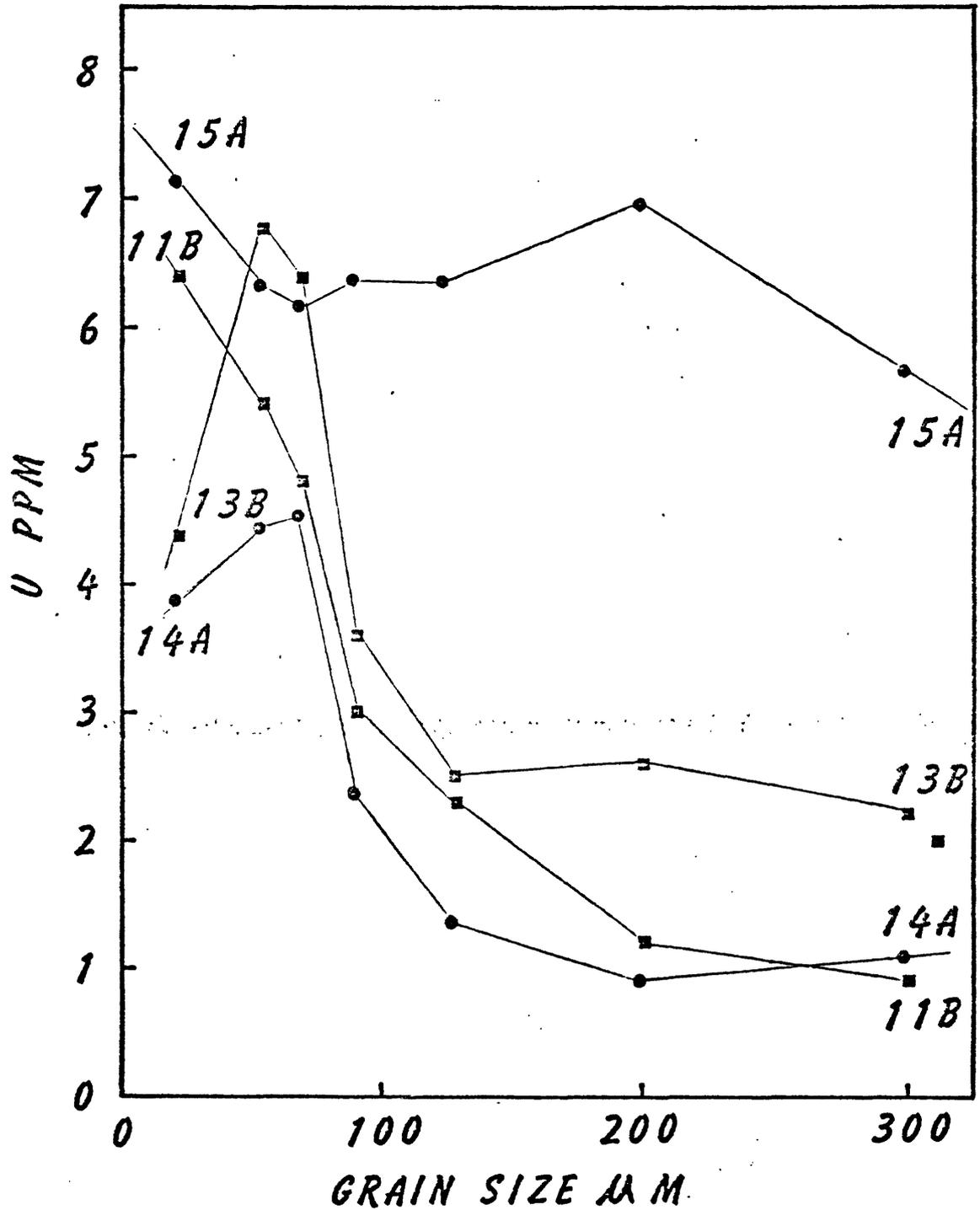


Figure 13C. Uranium concentration versus grain size in stream sediments.

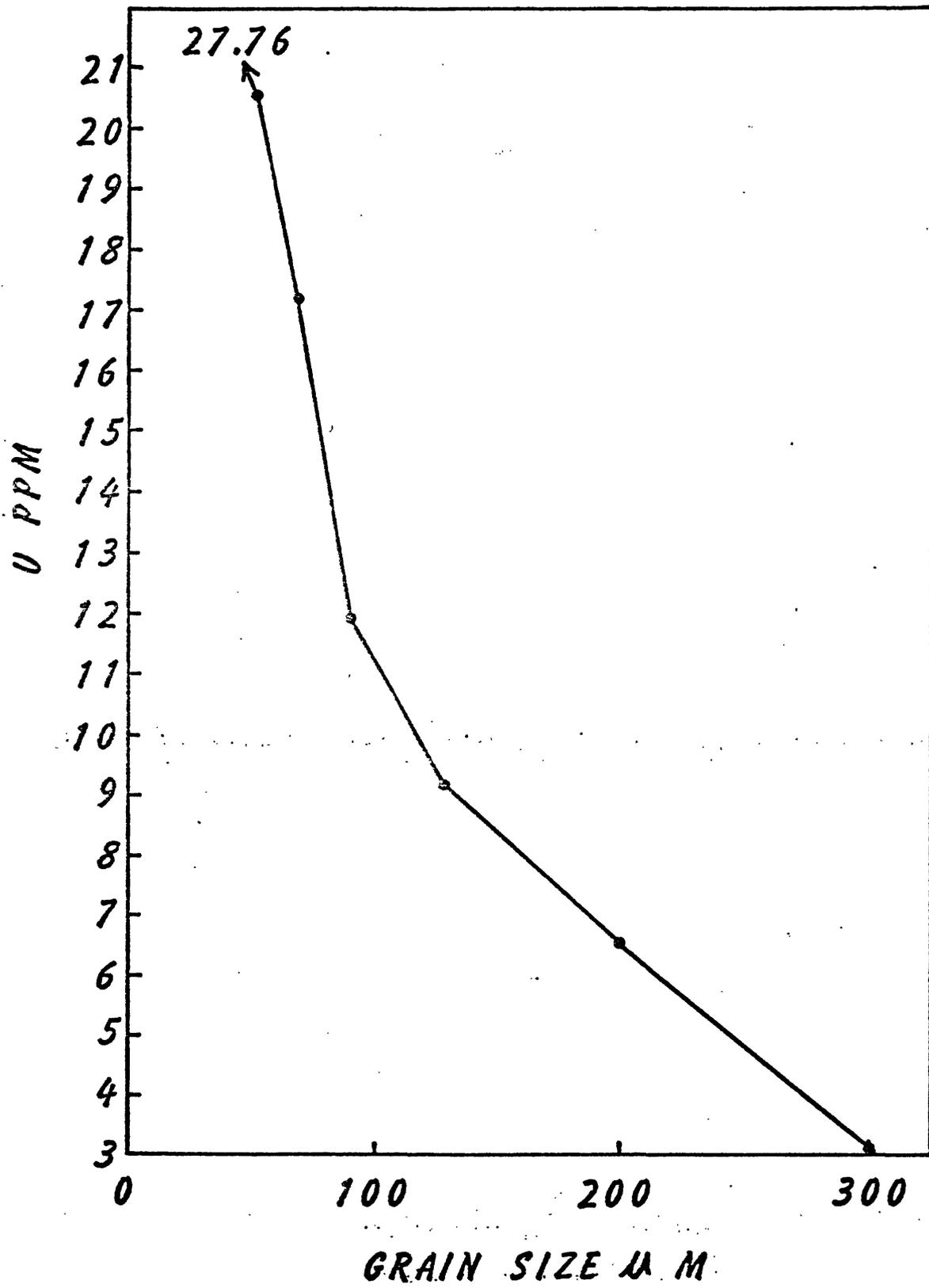


Figure 13D. Uranium concentration versus grain size in stream sediments.

TABLE 2

Uranium concentrations by grain-size (see page 18 for group sizes) for stream sediments taken at stations shown in Figure 1.

		Station Number							
		1-A	1-B	1-C	1-D	1-E	2-A	2-B	3-A
Grain-size	1	2.8	2.9	2.9	3.0	2.9		1.3	1.4
	2	2.5	2.2	2.1	2.2	2.5			1.3
	3	2.1	2.3	2.3	2.0	2.2	1.2	0.6	1.2
	4	2.2	2.3	2.6	1.8	2.1	1.4	1.2	1.5
	5	2.4		2.4	2.0	2.3	1.3	2.0	2.2
	6	2.6		2.9	2.2	2.4	1.9	2.4	2.8
	7	4.0		3.4	3.3	3.6	3.0	3.5	3.4
Group		Station Number							
		4-A	4-B	4-C	5-A	7-A	7-B	8-A	9-A
Grain-size	1	0.8	1.5	0.6		2.2	2.5	3.3	1.3
	2	0.7	0.6	0.6	1.9	1.5	1.4	3.4	2.8
	3	0.7		0.7	2.3	2.5	2.1	4.4	3.3
	4	1.0	0.9	1.5	2.3	3.8	3.2	4.2	4.4
	5	1.3	1.9	2.4	2.3	4.5	4.8	4.6	6.6
	6	2.4	5.0	5.3	2.6	5.2	6.3	4.6	10.1
	7	3.6	4.5	8.9	3.0	4.4	6.2	4.5	12.4
		Station Number							
		9-B	9-C	10-A	10-B	11-A	11-B	12-A	12-B
Grain-size	1	1.3	0.9	1.8	2.2	1.1	0.9	4.4	3.3
	2	4.0	2.4	3.1	3.9	1.3	1.2	3.5	3.2
	3	10.3	7.4	3.3	4.2	1.9	2.3	3.1	3.5
	4	14.0	9.2	4.5	5.7	2.8	3.0	3.2	3.7
	5	19.3	13.2	5.6	7.5	3.5	4.8	3.8	3.8
	6	14.7	12.5	6.5	7.1	4.1	5.4	3.2	4.1
	7	17.3	14.2	6.6	6.9	4.5	5.4	4.6	4.9
		Station Number							
		13-A	13-B	14-A	15-A	16-A			
Grain-size	1	2.3	2.2	1.1	5.7	3.1			
	2	2.7	2.6	0.9	7.0	6.6			
	3	3.3	2.5	1.4	6.4	9.2			
	4	3.7	3.6	2.4	6.4	12.0			
	5	4.0	6.4	4.5	6.2	17.2			
	6	3.7	6.8	4.5	6.3	20.6			
	7	3.5	4.4	3.9	7.1	27.8			

STATION NUMBER AND NAME	SAMPLE LOCATION WITHIN THE STREAM
1-A San Juan River, Colorado	Right bank 300 feet above gaging station above hot springs
1-B San Juan River, Colorado	Left bank above hot springs.
1-C San Juan River, Colorado	Left bank above hot springs
1-D San Juan River, Colorado	Left bank at spring overflow
1-E San Juan River, Colorado	Left bank in backwater area below hot springs
2-A Chinle Wash, Arizona	Composite taken at gaging station above diversion dam
2-B Chinle Wash, Arizona	Composite taken below diversion dam
3-A Cattle Tank, Chinle Wash, Arizona	Grab sample from within the tank
4-A Paria River, Arizona	Composite across the channel above gaging station
4-B Paria River, Arizona	Inside of meander above gaging station
4-C Paria River, Arizona	Outside of meander above gaging station
5-A Kaibab Lake, Arizona	Composite sample near shore
7-A Rio Puerco, New Mexico	Composite taken 1000 feet below gaging station
7-B Rio Puerco, New Mexico	Composite taken 1300 feet below gaging station
8-A Jemez River, New Mexico	Composite taken across channel at gaging station
9-A Cherry Creek, Colorado	Outside of meander, at bank undercut
9-B Cherry Creek, Colorado	Inside of meander above sampling site.
9-C Cherry Creek, Colorado	Composite taken across channel at sampling site
10-A Huerfano River, Colorado	Composite sample taken at sampling site
10-B Huerfano River, Colorado	Inside of meander 40 feet upstream of gaging station
11-A Coyote Creek, New Mexico	Composite sample taken at sampling site
11-B Coyote Creek, New Mexico	Inside of meander near gaging station
12-A Red River, New Mexico	At dam on right bank 15 feet below gaging station
12-B Red River, New Mexico	Below bridge, below dam right bank of stream
13-A Rio Ojo Caliente, New Mexico	From pool in stream near right bank of sampling site
13-B Rio Ojo Caliente, New Mexico	Below large boulders in main flow of stream
14-A Jemez River, New Mexico	Near sample site on right bank--outside of meander.
15-A Mineral Creek, Colorado	Composite taken above diversion dam near gaging station
16-A Rock Creek, Colorado	Composite of left and right banks at gaging station

<u>Group</u>	<u>Uranium Concentration</u>	<u>Weight of Split</u>
1	3.1 ppm	1036 gm
2	6.6	269
3	9.2	98
4	12.0	51
5	17.2	15
6	20.6	17
7	27.8	20

If everything finer than 60 mesh were analyzed, the sample would show a concentration of 9.5 ppm; this is not an unusually high value and would probably not be considered when isolating possible anomalous values, whereas the 27.8 ppm in the finest fraction would merit further investigation. Such skewness in grain size distributions of stream sediments toward the coarser fraction is not uncommon (in fact the skewness was more extreme in some of the samples), particularly in moderate to high gradient streams. Thus, it is strongly recommended that only particle-size fractions less than 90  $\mu\text{m}$  (170 mesh sieve) be used in order to avoid sample dilution (see figs. 13A-D).

Samples from the Paria River, with moderate uranium concentrations, show the greatest variation especially in the finest fraction. The inside and outside of the meander show very similar results except for the clay fraction. In this size range the uranium is sharply concentrated in the outside of the meander. This finding is unexpected, inasmuch as most sediment, including the heavy mineral fraction, is generally deposited on the inside of a meander. In the 44-63  $\mu\text{m}$  range, both the inside and the outside of the meander have the same uranium concentration, yet the concentration is less on the inside of the meander for the <44  $\mu\text{m}$  fraction than for the 44-63  $\mu\text{m}$  group; in the outside of the meander the <44  $\mu\text{m}$  fraction contains twice as much uranium as the 44-63  $\mu\text{m}$  fraction. From this, it can be assumed that ~~the velocity was sufficiently low to deposit some heavy minerals even in the~~ outside of the meander. The lower uranium concentration on the inside of

the meander is most likely not due to fewer heavy mineral grains containing uranium, but rather to a dilution effect by other small, but light-weight grains, such as clay minerals, which would be preferentially deposited in the slower moving waters of the inside of the meander. This suggests that the uranium present in this sample is not uranium adsorbed on clays, but rather uranium located in heavy minerals, such as apatite and rutile, and possibly in uranium minerals. This is substantiated by essentially no increase in Al with increase in uranium on the outside of the meander (hence, a low amount of clay) and a sudden increase in Al in the <44  $\mu\text{m}$  fraction on the inside of the meander.

#### Variations in other Elements with Uranium Concentration and Grain Size

A study of the increase or decrease in other elements between groups 6 and 7 size fractions (table 2) for the two locations in the Paria River meander gives a good estimate of which minerals may be a source of high uranium concentration, and which are not. It can be inferred from the chemical analyses that the major contributors of uranium are not clays (low Al content), carnotite (low K content), iron oxides or hydroxides (low Fe content), or uranium minerals rich in vanadium. The sudden increase in Zr suggests zircon as a significant contributor to the uranium content, although apatite is also likely; rutile, sphene, xenotime, monazite, and uraninite must also be considered.

Thus, chemical analysis of major and trace elements along with a petrographic analysis is a useful indicator of the possible sources of the uranium. For instance, a large Zr enrichment with the uranium is indicative of a concentration of zircon in the sediments but not particularly indicative of uranium deposits. On the other hand, an increase in uranium with ~~an increase in clay content (Al content) is suggestive of uranium leached~~

presumably from a moderate-sized uranium source--large enough to produce a stream sediment anomaly--being adsorbed onto the clays.

Other elements which show a characteristic increase with uranium for most of the sample sites are K, Mn, Mg, Ti, Ca, Al, Fe, Pb, Cr, Y, Zr, Li, Zn, Th, and As. The elements Cu, V, Ni, Se, and Na show increases for a few of the samples. Many of these elements may be used not only as indicators of the uranium host, but also as uranium pathfinders in situations where uranium may not have been leached in anomalous concentrations while its pathfinders were.

#### Comparison of Water and Stream Sediment Sampling

The correlation between uranium in water and stream sediments is not as good as might be expected (fig. 14). In general, the uranium concentration in stream sediments varies less between sample sites than the uranium concentration in water samples. In some cases a variation of two orders of magnitude for water results with no difference in the stream sediments, or in some instance anomalous stream-sediment uranium concentrations result with only a correspondingly moderate uranium concentration in water. Cherry Creek (Site 9) illustrates this latter case, where the sediment shows the highest value for this study and the water only a value close to the median for all the sample sites. The suspended material is also low in uranium, while the <44  $\mu\text{m}$  fraction of the sediments shows the highest uranium concentration. Part of this problem is a reflection of the inhomogeneities in stream sediments and the consequent sampling problem, as is illustrated by sample site 4 (fig. 14), while a more significant effect is that of the dependence of uranium in water on its solubility. Sample inhomogeneity is very minimal in filtered water samples, taken across the channel with a US DH-48 water sampler.

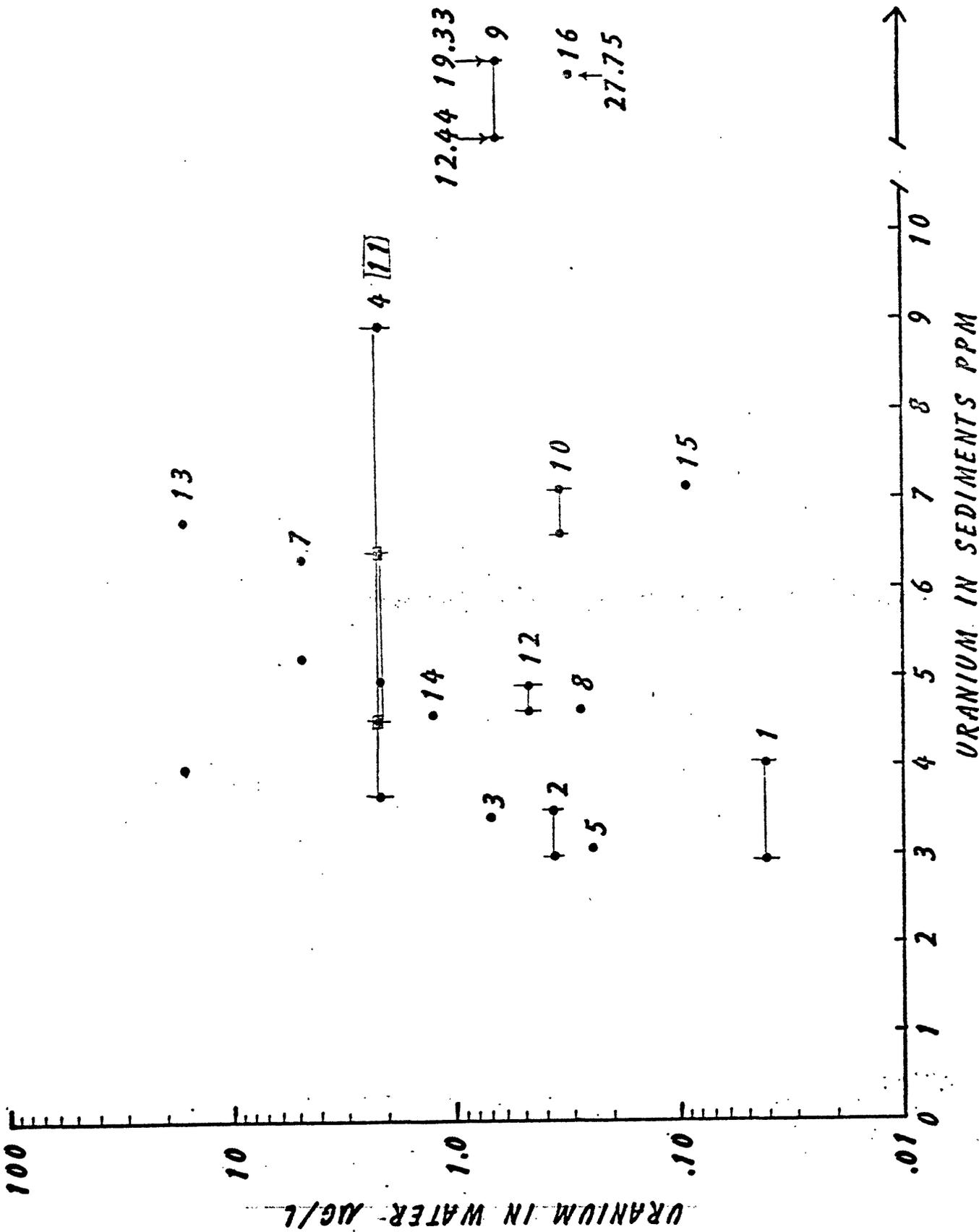


Figure 14. Uranium concentration in water versus uranium concentration in corresponding stream sediments. Numbers indicate sample site. All sediment sample values used are from either group 6 or group 7 size fractions.

Variations in the oxidizing environment may result in differential amounts of uranium in water or in the stream sediment. Thus, it is recommended that both water and stream sediment samples be taken in conjunction with each other.

### Conclusions

Optimum sampling methods for uranium exploration, utilizing surface waters and stream sediments have been established. For best results water samples should be taken using a US DH-48 water sampler across the stream channel. Samples for uranium analysis should be filtered and acidified in situ to minimize subsequent loss or gain of uranium and to maximize consistency from one type of geologic terrane to another and from one day to the next. The elements As, Ca, Al, B, Mg, K, and Na exhibit a positive correlation with uranium in surface waters.

A lack of correlation between concentrations of uranium in the dissolved and suspended fractions of water, and between either of them with stream sediments has been demonstrated, and it is apparent that to obtain the maximum information on uranium content of a stream it is necessary to analyze not only the water but also the corresponding suspended material (filtered in situ) and the stream sediments.

Studies on stream sediment sampling made in conjunction with water sampling show that the less than 90  $\mu\text{m}$  grain sizes are the optimum size fraction which minimizes the dilution effect of coarse sediment and maximizes the chances of detecting a uranium anomaly. A greater number of elements show a positive correlation with uranium in stream sediments than in water: K, Mn, Mg, Ti, Ca, Al, Fe, Pb, Cr, Y, Zr, Li, Zn, Th, and As.

Analyses have revealed that anomalies found in one of the three

fluvial system elements--dissolved and suspended constituents of water, and stream sediments--are frequently not reflected in the other two; hence, all three should be sampled and analyzed.

#### Acknowledgements

The author is grateful to Karen Noyce and Donna Collins for their patient assistance in the field from sunrise to sunset, and to Donna Collins and Sylvia Burnside for data compilation and assistance in the preparation of this manuscript; fission-track determinations of Mike Reimer are also greatly appreciated. Appreciation is also expressed to the Oak Ridge Gaseous Diffusion Plant, Oak Ridge, Tenn. (ORL), particularly to Gordon Cagle for assistance in obtaining fluorimetric determinations of uranium in water, and other elements in both water and stream sediments.

#### References Cited

- Barker, F. B., Johnson, J. O., Edwards, K. W., and Robinson, B. P., 1965, Determination of uranium in natural waters: U.S. Geol. Survey Water-Supply Paper 1696-C, 25 p.
- Guy, H. P. and Norman, V. W., 1970, Field methods for measurement of fluvial sediment: Techniques of Water Resources investigations of the U.S. Geological Survey. Book 3, Ch. C2, 59 p.