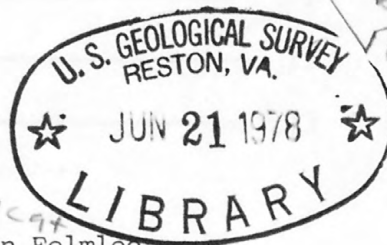UNITED STATES DEPARTMENT OF INTERIOR
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Uranium Values from Ion-Filter Water Sampling
Compared with Values from Bulk-Water Sampling

by

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ABSTRACT

Analytical values of uranium from well water sampled by means of
ion-filters were compared with analytical values of the same water
sampled by the standard bulk (1-liter) water-sampling technique (Brown,
Skougstad and Fishman, 1970). A fluorometric extraction method of
analysis was used on both sets of samples. Duplicate samples from
pumped wells in Pueblo County, Colorado were used.

Regression and correlation statistical analysis indicated that
while analytical results of the two sets of samples had a highly
significant correlation (r = 0.98), the ion-filter samples yielded only
20 percent as much uranium as the 1-liter water samples. It is possible
to predict U values from the ion-filter analysis results that would be
comparable with the values for the 1-liter samples, using the linear
regression formula. The predicted values, however, compared with the
1-liter values, using a chi-square test, were found to be significantly
different at the 5-percent level. Major deviations were found in two
pairs, 10 percent of the samples, suggesting that the predicted values
might be used if one were willing to accept the fact that an average of
10 percent of the samples would yield erroneous results. Sources of the
absolute deviations between the two sets of samples may lie in chemical
characteristics of the filters, or waters, or extraction method of the
analytical technique or some combination of these. The results of the
chi-square test also indicate that uranium values from at least 10

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percent of the ion-filter samples that we obtained, deviate
significantly from those obtained from the l-liter samples. Sources of
the deviations may lie in chemical characteristics of the filters, or
waters, or extraction technique, part of the analytical technique or
some combination of these.

INTRODUCTION

One of the newest methods proposed for sampling water for uranium
content is an on-site technique in which the water sample is filtered
through an ion-exchange resin or selective ion-filter disc. The filter
is then transported from the field to a laboratory for analysis. This
method has several logistical advantages over the method used by the
U.S. Geological Survey (USGS) as described by Brown, Skougstad and
Fishman (1970). The USGS method consists of collecting an unfiltered-
unacidified* or filtered-acidified l-liter sample of water which is
transported to a laboratory for analysis. Advantages of the ion-filter
are: (1) The uranium is concentrated on site in a filter disk; (2) No
acidification is necessary; (3) No danger of uranium being lost through
reaction with a plastic container during transport or storage before
analysis; (4) Field handling of boxes full of bulky l-liter sample
bottles is eliminated; (5) Costs of shipping or transporting hundreds of
liters of water to the laboratory are eliminated; (6) Danger of sample
loss, uranium loss, or some contamination in laboratory handling of l-
liter samples is eliminated.

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*The USGS never collects unfiltered-acidified samples.

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Mention or display of trade names in this report is not to be construed as an endorsement by the USGS of such companies or their products.

METHODS

Sampling: To compare the values for uranium determined in samples collected by the two methods, twenty duplicate samples were collected in the field and analyzed at the USGS Branch of Analytical Laboratories, Reston, Virginia. Twenty ion-filters were purchased from a private manufacturer and supplier, Environmental Devices Corporation (ENDECO). To collect the ion-filter samples we used a clear plastic sampling kit (fig. 1) furnished by ENDECO, consisting of a filter unit with ion-filter holder, calibrated reservoir, and vacuum pump. Samples were collected at 20 localities in Pueblo County, Colo. (fig. 2) in an area where many pumped wells produce water reported by Richard Gamewell, Pueblo County Health Physicist (written commun., 1975) to contain significant quantities of uranium.

Well-water samples were collected as near the pump as possible, by-passing surge tanks, pressure tanks, water softeners and other treatment facilities. Water was filtered through a $0.45 \mu m$-filter at each sample site. One liter of the filtrate was collected in a 1-liter sample bottle and acidified with 3 ml of 6N nitric acid. A second increment of filtrate was collected in another sample bottle and 200 ml of it was poured into the calibrated reservoir of the ion-filter sampling kit. The water sample was drawn through the ion filter by the vacuum pump. Guidance in the use of the ion-filter sampling technique was furnished by a representative of the supplier, W. B. Kerfoot, who

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Figure 1.- Ion-filter sample-collecting kit. A 200-ml. sample of water is added to the upper
calibrated reservoir. Ion filter and prefilter are located in a holder at the base of the reservoir.
A slight vacuum is created and maintained in the 500 ml. graduated cylinder by means of the hand
vacuum pump until the water sample has passed through the filter. The ion filter is removed
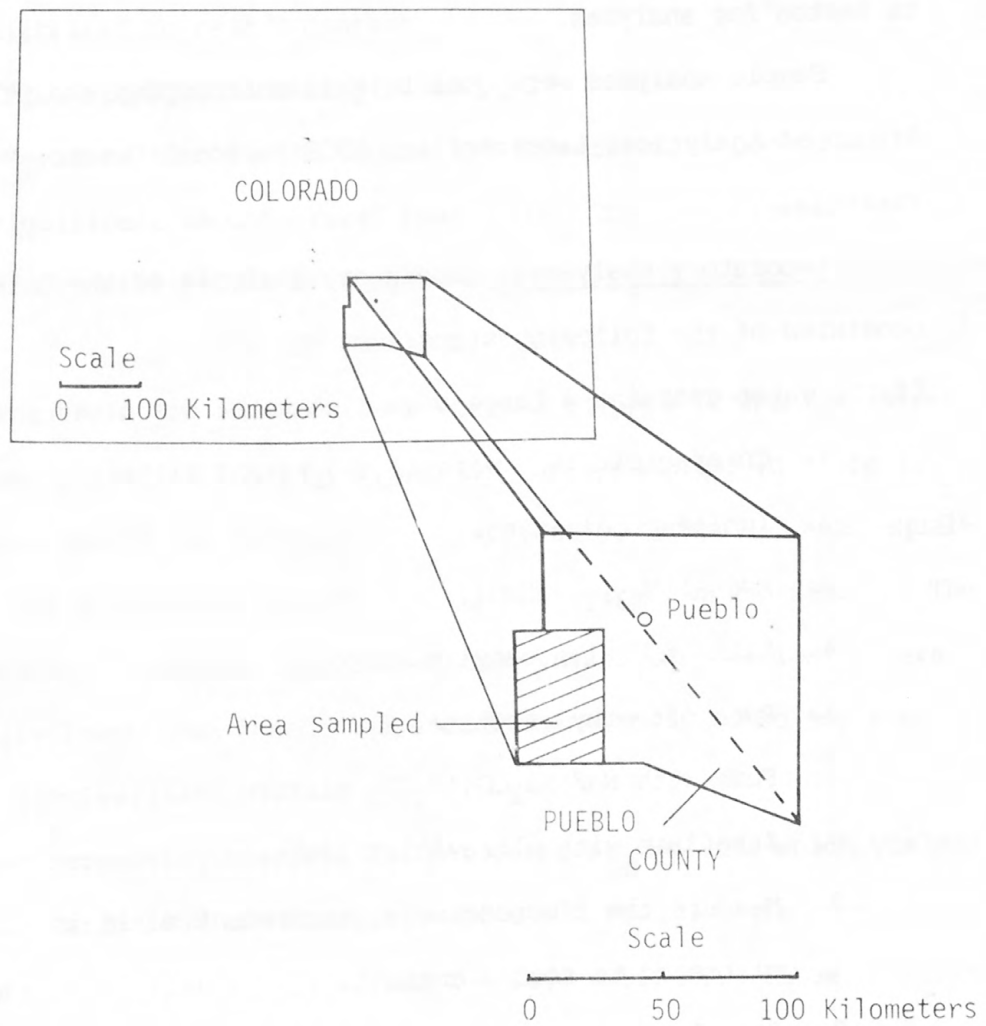with tweezers and stored in an individual plastic storage vial.

Figure 2.-Location of area (cross-hatched) of sampled wells in
Pueblo County, Colorado.

accompanied Survey personnel to the field.

The 20 1-liter water samples were crated and shipped to Reston. The duplicate iron-filter samples in vials, which fit easily into a plastic envelope, were renumbered in randomized fashion and also mailed to Reston for analyses.

Sample analyses were done by Marian Schnepfe, analytical chemist, Branch of Analytical Laboratories, USGS National Center, Reston, Virginia.

Laboratory Analyses: Laboratory analysis of the bulk water sample consisted of the following steps:

If the water contains a large amount of total dissolved solids,

1. Co precipitate U with $Al_2(PO_4)_3$ and filter.

2. Ignite precipitate.

3. Add $Al(NO_3)_3$ + HNO_3.

4. Extract U with ethyl acetate.

5. Burn off ethyl acetate.

6. Fuse with $NaF \cdot Na_2CO_3 \cdot K_2CO_3$ mixture (pill).

7. Irradiate with ultraviolet light.

8. Measure the fluorescence; measurement scale is directly calibrated to read U content.

9. Calculate U content.

If the water contains a small amount of dissolved solids,

1. Evaporate to dryness

   Followed by steps 3, 4, 5, 6, 7, 8, and 9 above.

Analysis of the resin ion filters consisted of the following steps:

1. Extract U from filter with 4 ml of 20% HNO_3

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2. Transfer leachate to platinum dish.

3. Fuse with $NaF \cdot Na_2CO_3 \cdot K_2CO_3$ pill.

4. Irradiate with ultraviolet light.

5. Measure the fluorescence; measurement scale is directly calibrated to read U content.

6. Calculate U content of pill as $\mu g/l$.

Analyses were also run on unused ion filters which proved to contain insignificant amounts (.005 ppb) of U. The lower reporting limit was arbitrarily set at 0.04 $\mu g/l$.

DATA AND COMPARATIVE TESTS

Raw data from the analyses recalculated to present uranium values in micrograms per liter (parts per billion) are presented in table 1. The data were tested for correlation, graphically, using a linear equal-value-line and logarithmic-scaled correlation scatter-gram, fig. 3. The graph and table 1 indicate that the uranium values for the ion-filters are generally lower than the corresponding values determined for the bulk water samples.

Linear regression analysis was performed on the data which yielded (table 1) a coefficient of correlation of $r = 0.98$ and regression formulas of: $Y = -0.31 + 0.19 \, X$, and $X = 1.60 + 5.14 \, Y$. These measurements indicated a parallel relationship between the two data sets, but the ion-filter values average less than 20 percent of the bulk-water sample values.

The Chi Square (χ^2) relationship (examples: Griffiths, 1967, p. 345) was used to determine if valid (1-liter-sample) values of $\hat{X}$ could be predicted from the (ion-filter-sample) values of Y because of the

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Table 1.--Uranium data from the analysis of duplicate samples of well water.

[Values are given in micrograms per liter or, roughly, parts per billion. $\hat{X}, \hat{Y}$: Values of $\hat{X}$ and $\hat{Y}$ predicted from regression formula.]

Sample No.	Bulk-water samples U(µg/liter) X	Ion-filter samples U(µg/liter) Y	Predicted values U(µg/liter) $\hat{X}$	$\hat{Y}$
MS 77-34	3.6	.29	3.18	.37
-35	180	36	192.69	33.61
-36	77	9.0	49.40	14.20
-37	3.1	.88	6.31	.28
-38	6.2	.68	5.25	.85
-39	8.8	2.3	13.85	1.35
-40	.03	[.02]	1.75	-.30
-41	.34	.15	2.44	-.24
-42	2.2	.38	3.66	.11
-44	.05	[.02]	1.75	-.30
-45	19	.88	6.31	3.27
-46	2.6	.78	5.78	.18
-47	3.8	.50	4.29	.41
-48	4.2	.97	6.79	.48
-49	.29	[.02]	1.75	-.25
-50	2.4	.56	4.61	.14
-51	5.7	1.0	6.95	.77
-52	.04	[.02]	1.75	-.30
-61	2.6	[.02]	1.75	.18
-62	.02	[.02]	1.75	-.31

Note: Values of [.02] are arbitrary values substituted for values reported as $\leq$.04, to permit their use in statistical analysis.

Coefficient of determination $(r^2)=.97$ Correlation coefficient $(r)=.98$

Regression formulas: $\hat{Y}= -.31 + .19X$
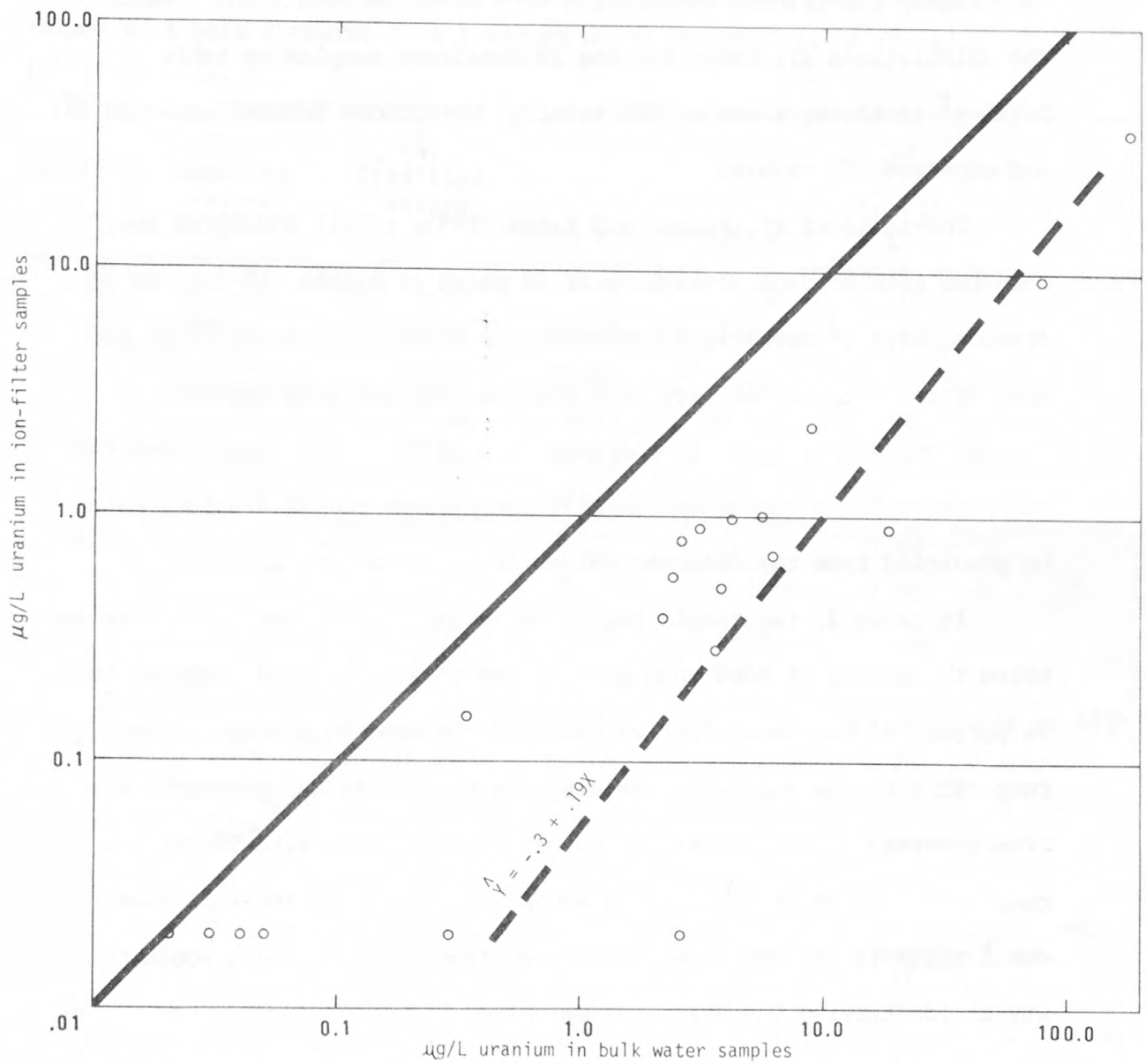
$\hat{X}= 1.60 +5.41Y$

Figure 3.-Logarithmic scale scatter diagram of correlation points of ion-
filter U values (Y) and bulk-water analytical U values (X) shown in table 1.
Logarithmic bases were used to compensate for problems of scale. The solid
diagonal line is an equal value line along which points of Y=X values would plot.

very highly significant correlation (r = 0.98) between X and Y values. The calculations are shown for the 20 duplicate samples on table 2. Total χ^2 is 60.68, a sum of the total χ^2 deviations between expected ($\hat{X}$) and observed (X) values.

The table of χ^2 (Fisher and Yates, 1953, p. 41) indicates that when two sets of data consisting of 20 pairs of values (19 degrees of freedom) have χ^2 deviations between pairs producing a total χ^2 of more than 30.14. The probability that the two sets are from the same population is less than five percent (p = <0.05). The results indicate that acceptable accurate values of X (bulk-water-sample uranium) cannot be predicted from the observed values of Y (ion-filter uranium).

In table 2, two sample pairs (10 percent of the data) are noted as being the source of more than half of the total χ^2. This suggests that 90 percent of the ion-filter values could be used to produce values comparable to the bulk-water values. In this instance, predictions of X from observed Y, the ion filter values could be used with 90 percent confidence. That is to say, one would have to accept the fact that one $\hat{X}$ value in ten would be completely erroneous, and there would be no way of identifying the erroneous values.

Table 2.--Chi square (χ^2) test of values of $\hat{X}$ predicted from values of Y. Values of X were computed from Y values using the regression formula: $\hat{X}=1.60 + 5.41Y$.

Sample No.	(X) Observed values O	($\hat{X}$) Predicted values E	O-E	$(O-E)^2$	χ^2 $\dfrac{(O-E)^2}{E}$
-35	3.6	3.18	.42	.18	.06
-36	180	192.69	-12.69	161.04	.84
-37	77	49.40	27.60	761.76	15.42-Source of high χ^2
-38	3.1	6.31	-3.21	10.30	1.63
-39	6.2	5.25	.95	.90	.17
-40	8.8	13.85	-5.05	25.50	1.84
-41	.03	1.75	-1.72	2.96	1.69
-42	.34	2.44	-2.10	4.41	1.81
-43	2.2	3.66	-1.46	2.13	.58
-44	.05	1.75	-1.70	2.89	1.65
-45	19	6.31	12.69	161.04	25.52-Source of high χ^2
-46	2.6	5.78	-3.18	10.11	1.75
-47	3.8	4.29	-0.49	.24	.06
-48	4.2	6.79	-2.59	6.71	.99
-49	.29	1.75	-1.46	2.13	1.22
-50	2.4	4.61	-2.21	4.88	1.06
-51	5.7	6.95	-1.25	1.56	.22
-52	.04	1.75	-1.71	3.92	1.67
-61	2.6	1.75	.85	.72	.41
-62	.02	1.75	-1.73	2.99	1.71

Total χ^2--60.30

Note: For 19 d.f., total χ^2 of more than 30.14 has the probabilty of occurrence of less than 5 percent (P<.05) of the time in the same normal population.

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It is our opinion that the ion-filter method of sampling yields uranium values that are proportionally too low for uranium exploration purposes. All of the bulk samples contained U at detectable levels; six of the ion-filter samples did not. Nor can values obtained be depended on to predict accurately with more than 90 percent confidence, the higher values obtained by bulk-water sampling.

Marian Schnepfe, analyst, (oral commum., 1977) suggests two possible causes for the low values obtained from the ion filters. One, that the filter may go into a type of equilibrium reaction with the uranium in the water being filtered whereby the ion filter can absorb only a proportional increment of the uranium (20%). Two, the recommended method of extracting the uranium from the filter in the laboratory calls for one extraction. This may not be enough. A better analytical method might be to perform two or more successive extractions from each filter.

The advantages of the use of ion-filters are desirable, but the results of this test suggest that there are unsolved problems remaining either in the sampling, or the extraction of the U from the filter, or both. Assuming that the bulk-water sample analyses are relatively accurate in view of the special care taken with these samples, ion-filter values could be used for reconnaissance purposes if the 10 percent error rate were acceptable, and analytical values (Y) were converted using the formula: $\hat{X} = 1.60 + 5.41\ Y$.

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