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# Strontium-90 Determinations by Cerenkov Radiation Counting for Well Monitoring at Oak Ridge National Laboratory

Ingvar L. Larsen

ENVIRONMENTAL SCIENCES DIVISION
Publication No. 1701

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NUCLEAR WASTE PROGRAMS
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# ABSTRACT

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A rapid method for determination of $^{90}$Sr (28.8 y half-life) via its daughter $^{90}$Y (64.1 h half-life) in aqueous samples from the solid low-level radioactive waste disposal areas at the Oak Ridge National Laboratory (ORNL) utilized the principle of direct Cerenkov radiation counting. This technique is applicable for beta particles exhibiting maximum energies greater than 0.42 pJ (263 keV) in aqueous solution. In the presence of other contributing energetic beta emitters the technique may serve as a useful screening method to distinguish low activity samples from more moderate or higher activity concentrations.

A comparison between analysis of $^{90}$Sr by Cerenkov radiation counting and by standard wet chemical separation techniques indicated a high degree of correlation and excellent agreement.

The detection limit for a 20-mL sample under the prescribed experimental conditions and a counting interval of 20 min was approximately 0.2 dpm/mL (0.1 pCi/mL).

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# INTRODUCTION

Water samples collected from monitoring wells located within and near the solid low-level radioactive waste disposal areas at Oak Ridge National Laboratory (ORNL) have been routinely analyzed for radioactivity. These analyses include gross alpha, gross beta, $^{90}Sr$, and $^{3}H$ determinations and gamma-spectrometric scans for such radionuclides as $^{60}Co$ and $^{137}Cs$. Several hundred samples collected quarterly produced an analytical backlog in the $^{90}Sr$ measurements that frequently prevented rapid assay and caused corresponding delays in experimental work. This delay was attributed to the low priority status assigned to these samples; other ORNL investigations often took precedence.

The purpose of this report is to demonstrate the feasibility of using Cerenkov radiation counting to evaluate $^{90}Sr$ concentration levels in aqueous samples collected from within and near the nuclear waste disposal areas at ORNL.

The established methodology for $^{90}Sr$ determination in aqueous samples at ORNL involves chemical separation and therefore the use of skilled technicians to perform the analyses. The process requires the addition of strontium carrier to the sample, its precipitation as the insoluble carbonate, and its separation from calcium and magnesium by nitrate precipitation in fuming nitric acid, followed by acetone washes. Further purification is accomplished by removing impurities with mixed-rare-earth hydroxide scavenging and by removing barium as the chromate. Final purification is made by precipitating strontium as the oxalate, which is then beta counted using a low background beta counter (T. Scott, 1980, Analytical Chemistry Division, ORNL, personal communication; ORNL Master Analytical Manual, 1957). This series of treatments, which was required for accurate $^{90}$Sr determinations, contributed appreciably to the delay in the analysis. In an attempt to alleviate the $^{90}$Sr analysis backlog and to more rapidly assess $^{90}$Sr concentrations, the feasibility of using direct Cerenkov radiation counting techniques (Haberer 1966, Ross 1969, Carmon 1979) was investigated. Cerenkov radiation counting is applicable for beta particles in aqueous solution exhibiting maximum energies greater than 0.042 pJ (0.263 MeV) (Ross 1969). Strontium-90 (28.8 y half-life) exhibits an intermediate beta energy maximum [0.087 pJ (0.546 MeV)], while its daughter $^{90}$Y (64.1 h half-life) has a high maximum beta energy (2.28 MeV), which facilitates its determination by Cerenkov radiation counting.

Limitations occur in application of Cerenkov radiation counting for $^{90}$Sr. Cerenkov radiation counting cannot resolve mixtures containing beta emitters of similar maximum energies. The use of electronic discriminators or "window settings" may be necessary to eliminate interference from low-energy beta emitters. In the presence of beta particles that have similar energy but arise from different nuclides, a biased signal may result.

The aqueous samples from the monitoring wells may contain, in addition to any $^{90}$Sr, other artificial radionuclides of medium half-life such as $^{137}$Cs and $^{60}$Co. The presence of these radionuclides in samples and their effects on Cerenkov radiation counting for $^{90}$Y determinations are illustrated in Table 1a. Approximately

Table 1a. Effects of $^{137}$Cs and $^{60}$Co on $^{90}$Sr ($^{90}$Y) determinations by Cerenkov radiation counting[a]

| Radionuclides | Activity added (dpm) | Average net count rate[b] (cpm) | Calculated $^{90}$Sr activity (dpm) | Relative contributions from $^{137}$Cs and/or $^{60}$Co $\frac{^{90}\text{Sr calc.} - {}^{90}\text{Sr added}}{^{90}\text{Sr added}}$ |
|---|---|---|---|---|
| $^{90}$Sr | 1037 ± 12 | 385 ± 9 | 1026 ± 25 | -- |
| $^{137}$Cs | 991 ± 15 | 13.9 ± 0.3 | 37.0 ± 0.8 | -- |
| $^{60}$Co | 965 ± 12 | 45.8 ± 1.9 | 122 ± 5 | -- |
| $^{137}$Cs + $^{60}$Co | 991 + 965 | 57.3 ± 1.1 | 153 ± 3 | -- |
| $^{137}$Cs + $^{90}$Sr | 991 + 1037 | 399 ± 6 | 1063 ± 16 | 2.5% |
| $^{60}$Co + $^{90}$Sr | 965 + 1037 | 427 ± 1 | 1138 ± 3 | 9.7% |
| $^{137}$Cs + $^{60}$Co + $^{90}$Sr | 991 + 965 + 1037 | 438 ± 6 | 1167 ± 15 | 12.5% |

Instrument settings as follows (Packard Tricarb liquid scintillation counter model 3225 coincident mode operation):

Discriminator window settings: 325-1000
High voltage: 1814 ± 50 V
Amplifier gain: 48%
Sample volume: 20 mL

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[a] All values are ± 1 SD.
[b] Average and SD of duplicate samples.

Table 1b. Decay properties of selected radionuclides

| | Half-life | $\beta^-$ max. MeV[a] | MeV[a] | Max. Compton electron energy MeV[b] (neglecting binding energy) |
|---|---|---|---|---|
| $^{60}$Co | 5.2 y | 0.318 | 1.33<br>1.17 | 1.12<br>0.96 |
| $^{137}$Cs | 30.2 y | 0.514 (94%)<br>1.18 (6%) | 0.662 | 0.48 |
| $^{90}$Sr | 28.8 y | 0.546 | | |
| $^{90}$Y | 64.1 h | 2.28 | | |

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[a] 1 MeV = 0.1602 pJ.
[b] Calculated from Eq. 4.2 in National Council on Radiation Protection and Measurement, 1978, A Handbook of Radioactivity Measurements and Procedures, NCRP Report No. 58, Washington, D.C.

equal activities of $^{137}Cs$ and/or $^{60}Co$ were added to test solutions containing $^{90}Sr$. Under the experimental conditions, the presence of $^{137}Cs$ contributed less than 3% to the $^{90}Sr$ determination, whereas $^{60}Co$ contributed approximately 10% to the calculated $^{90}Sr$ content. Although $^{60}Co$ has a lower maximum beta energy [0.05 pJ (0.318 MeV)] than $^{137}Cs$ [0.082 pJ (0.514 MeV max)], its influence may be attributed to the more energetic Compton electrons (Table 1b). Typically, $^{60}Co$ concentrations are less than 1 dpm/mL for the monitoring wells, although occasionally higher concentrations are encountered. When necessary, corrections for $^{60}Co$ interferences can be made following a gamma spectrometric analysis (Reynolds and Eldridge 1980). False positive signals arising from other contributing radionuclides can be tolerated in screening applications; and false negative signals are not possible except under conditions of extreme color quenching.

Additional limits to Cerenkov radiation counting can be caused by color quenching or by suspended material, both of which interfere with light transmission from the sample to the detector. These deficiencies, however, can be overcome when necessary by using the internal standard additions method which involves adding a minuscule known amount of $^{90}Sr$ ($^{90}Y$) to the solution after an initial count and recounting to determine an efficiency factor for the quenched solution. Samples collected from monitoring wells are filtered prior to analysis, minimizing suspended particulate effects. The probability of color quenching can be assessed by visual inspection; samples that appear colored should be checked for counting efficiency via the internal standard methods.

## ANALYTICAL COMPARISONS

A comparison between the standard ORNL chemical separation technique and that of the Cerenkov radiation counting method was performed on 42 samples from ORNL waste disposal areas. Samples for Cerenkov radiation counting consisted of 20 mL of well water (subsampled from a large container after allowing sufficient time to reach secular equilibrium) directly pipetted into plastic liquid scintillation vials without any scintillation cocktail and counted for 20 min. A blank composed of 20 mL of distilled water was used to correct for instrumental background contributions. The net count rates of the samples were then converted to disintegrations per minute using a counting efficiency calculated from a standard of $^{90}$Sr ($^{90}$Y in secular equilibrium) of the same volume. The concentration range of the 42 samples spanned four orders of magnitude. The results of this comparison of the two methods are given in Table 2.

The data reported in Table 2 are expressed to the nearest 0.1 dpm unless concentrations exceeding 99.9 dpm are encountered, in which case the values are rounded to three significant figures. The Cerenkov counting efficiency in this analysis was approximately 48%. The detection limit under the specified counting condition, which is defined as the lowest concentration that can be present in the sample in order to report a positive value 95% of the time after correcting for background interferences (Altshuler and Pasternack 1963, Pasternack and Harley 1971), is approximately 0.2 dpm/mL. The reported uncertainty terms are counting errors of one standard deviation.

Table 2. Comparison between $^{90}Sr$ determinations by the method of Cerenkov radiation counting and standard analytical methodology (sample concentrations arranged in descending order)(dpm/ml)

| Sample number | Cerenkov | ± SD | Analytical | ± SD | Cerenkov/analytical | Logarithm of ratio | Cerenkov minus analytical |
|---|---|---|---|---|---|---|---|
| 1 | 2395.0 | 3.40 | 2370.00 | 30.00 | 1.01055 | 0.01049 | 25.00 |
| 2 | 824.0 | 2.10 | 910.00 | 5.00 | 0.90549 | -0.09927 | -86.00 |
| 3 | 715.0 | 1.90 | 720.00 | 5.00 | 0.99306 | -0.00697 | -5.00 |
| 4 | 335.0 | 1.20 | 338.00 | 3.00 | 0.99112 | -0.00892 | -3.00 |
| 5 | 215.0 | 1.00 | 197.00 | 2.00 | 1.09137 | 0.08743 | 18.00 |
| 6 | 204.0 | 1.00 | 204.00 | 2.50 | 1.00000 | 0.00000 | 0.00 |
| 7 | 158.0 | 0.90 | 162.00 | 2.00 | 0.97531 | -0.02500 | -4.00 |
| 8 | 124.0 | 1.30 | 131.00 | 2.00 | 0.94656 | -0.05492 | -7.00 |
| 9 | 105.0 | 0.70 | 106.00 | 1.00 | 0.99057 | -0.00948 | -1.00 |
| 10 | 101.0 | 0.70 | 97.00 | 1.00 | 1.04124 | 0.04041 | 4.00 |
| 11 | 77.7 | 0.60 | 84.00 | 1.00 | 0.92500 | -0.07796 | -6.30 |
| 12 | 67.7 | 1.10 | 62.00 | 0.50 | 1.09194 | 0.08795 | 5.70 |
| 13 | 66.4 | 1.10 | 71.00 | 0.50 | 0.93521 | 0.06698 | -4.60 |
| 14 | 57.5 | 0.50 | 54.00 | 0.50 | 1.06481 | 0.06280 | 3.50 |
| 15 | 56.4 | 0.50 | 55.00 | 0.50 | 1.02545 | 0.02514 | 1.40 |
| 16 | 47.5 | 0.50 | 46.00 | 0.50 | 1.03261 | 0.03209 | 1.50 |
| 17 | 35.3 | 0.40 | 34.00 | 0.50 | 1.03824 | 0.03752 | 1.30 |
| 18 | 32.2 | 0.40 | 31.00 | 0.50 | 1.03871 | 0.03798 | 1.20 |
| 19 | 31.3 | 0.40 | 31.00 | 0.50 | 1.00968 | 0.00963 | 0.30 |
| 20 | 30.9 | 0.40 | 29.00 | 0.50 | 1.06552 | 0.06346 | 1.90 |
| 21 | 28.2 | 0.40 | 26.00 | 0.50 | 1.08462 | 0.08123 | 2.20 |
| 22 | 24.9 | 0.40 | 24.00 | 0.50 | 1.03750 | 0.03681 | 0.90 |
| 23 | 8.0 | 0.20 | 6.60 | 0.20 | 1.21212 | 0.19237 | 1.40 |
| 24 | 7.5 | 0.20 | 6.90 | 0.15 | 1.08696 | 0.08338 | 0.60 |
| 25 | 6.9 | 0.20 | 6.70 | 0.10 | 1.02985 | 0.02941 | 0.20 |
| 26 | 4.9 | 0.20 | 2.20 | 0.05 | 2.22727 | 0.80078 | 2.70 |
| 27 | 4.7 | 0.20 | 4.60 | 0.10 | 1.02174 | 0.02151 | 0.10 |
| 28 | 3.1 | 0.15 | 2.60 | 0.10 | 1.19231 | 0.17589 | 0.50 |
| 29 | 2.9 | 0.15 | 3.00 | 0.15 | 0.96667 | -0.03390 | -0.10 |
| 30 | 2.9 | 0.15 | 2.90 | 0.05 | 1.00000 | 0.00000 | 0.00 |
| 31 | 2.7 | 0.10 | 2.80 | 0.10 | 0.96429 | -0.03637 | -0.10 |
| 32 | 1.8 | 0.10 | 1.80 | 0.05 | 1.00000 | 0.00000 | 0.00 |
| 33 | 1.8 | 0.10 | 1.80 | 0.05 | 1.00000 | 0.00000 | 0.00 |
| 34 | 1.6 | 0.10 | 1.60 | 0.05 | 1.00000 | 0.00000 | 0.00 |
| 35 | 1.6 | 0.10 | 1.40 | 0.05 | 1.14286 | 0.13353 | 0.20 |
| 36 | 1.3 | 0.10 | 1.70 | 0.05 | 0.76471 | -0.26826 | -0.40 |
| 37 | 0.9 | 0.10 | 1.30 | 0.05 | 0.69231 | -0.36772 | -0.40 |
| 38 | 0.9 | 0.10 | 0.82 | 0.05 | 1.09756 | 0.09309 | 0.08 |
| 39 | 0.4 | 0.10 | 0.54 | 0.02 | 0.74074 | -0.30010 | -0.14 |
| 40 | 0.4 | 0.10 | 0.41 | 0.04 | 0.97561 | -0.02469 | -0.01 |
| 41 | 0.2 | 0.10 | 0.32 | 0.04 | 0.62500 | 0.47000 | -0.12 |
| 42 | 0.2 | 0.10 | 0.26 | 0.01 | 0.76923 | -0.26236 | -0.06 |
| | | | | Mean | 1.01914 | 0.000714 | -1.08452 |
| | | | | SD | 0.22570 | 0.184520 | 14.4359 |
| | | | | SE | 0.03483 | 0.028472 | 2.22751 |

1 Bq = 1 dps = 60 dpm = 27.03 pCi

Concentrations reported in Table 2 for analytical radiochemical results refer to the determinations performed by the standard chemical separation procedures previously described. These determinations were made on $^{90}Sr$ before ingrowth of activity of its daughter $^{90}Y$. Sample counting time is nominally 20 min. Detection limits are approximately 1 dpm of $^{90}Sr$ per sample, which corresponds to approximately 0.002 dpm/mL for a 500-mL sample. The data are usually reported with two significant figures for values less than 100 dpm/mL and with three significant figures for concentrations exceeding 100 dpm/mL. The reported uncertainty terms are counting errors of one standard deviation. (Table 3 summarizes the analytical conditions for the two methods of analysis.)

The precision terms reported in Table 2 are not expected to be identical because they are based on "counting statistics" and are, therefore, functions of the sample size, concentration, counting efficiency, and counting time of each particular analytical technique. Rather, these terms reflect the expected reproducibility for a given sample and the experimental conditions under which it was determined.

## STATISTICAL EVALUATION

The paired observations can be statistically evaluated using a Student-t test to determine if a significant difference exists between the two methods for the paired sample determinations. Several options in using this test are available and include:

(1) testing the overall mean of the differences of each pair for significance from zero;

Table 3. Summary of the analytical conditions for Cerenkov radiation counting and chemical separation techniques for $^{90}$Sr determination

| | Cerenkov radiation counting | Chemical separation techniques |
|---|---|---|
| Instrument | Liquid scintillation counter | Gas flow low-background beta counter |
| Procedures | Direct counting (coincident mode) | Chemical precipitation |
| Sample container | 25-ml plastic scintillation vial | Card mounted filter paper |
| Sample volume required | 10-20 mls | 100-500 mls |
| Sample preparation time | ∿5 min | ∿8 h |
| Counting time | 20 min | 20 min |
| Number of samples processed per day | ∿70 | ∿24 |
| Background CPM | ∿5-10 | ∿0.5 |
| Detection limit | ∿0.2 dpm/ml | 1 dpm/sample (0.01-0.002 dpm/ml) |
| Detection efficiency | ∿40-50% | ∿25% |

(2) testing the overall average ratio of each pair for significance from unity; or

(3) testing the overall average of the logarithm of the ratio of each data pair for significance from zero (which is the same as testing the average difference between logarithms of the data pairs).

Because the ranges in concentrations covered four orders of magnitude, and because a greater absolute difference is expected between larger quantities than between smaller quantities, the test was applied to logarithms of the ratio of the paired observations. This treatment tends to "normalize" any extreme magnitudes occurring in differences over low to high concentrations.

In using the Student-t test, the differences in individual pairs are assumed to be distributed about some mean that represents the average of the difference in the effects of the two treatments over the population of which these pairs are considered random samples (Snedecor and Cochran 1967). The differences are assumed to be random, normally and independently distributed, with a population mean of zero. Using coded index values (Barnett 1975), the logarithms of the ratios of the paired observations can be shown to approximately follow these assumptions.

The Student-t test is given as follows (Snedecor and Cochran 1967):

$$t = \frac{\bar{D} - 0}{S_{\bar{D}}} , \quad S_{\bar{D}} = \frac{S_D}{\sqrt{n}} , \quad S_D = \sqrt{\frac{\Sigma(Di - \bar{D})^2}{n - 1}} ,$$

where

$D_i$ = logarithm of the ratio of the data pairs,

$\bar{D}$ = sample average of the ratios,

$n$ = number of data pairs, and

$n - 1$ = degrees of freedom (d.f.).

From the mean and standard error of the logarithm of the ratio of the concentration by the two methods (Table 2), the calculated t value is

$$t = \frac{0.000714 - 0}{0.028472} = 0.02508 \quad .$$

A comparison of the above calculated t value with tabulated Student-t values with 41 d.f. indicates no significant difference in the $^{90}Sr$ determinations between the two methods, not only at the 5% probability level but even at a significance level as large as 40%.

## LINEAR REGRESSION

Linear regression analysis was applied to examine the degree of correlation between the data sets. The Cerenkov radiation values were considered the dependent variable and the results from the standard analytical method were considered the independent variable. The parameters examined included the correlation coefficient, slope, and intercept values. A plot of the residuals (observed dependent value minus the predicted value) was also examined to verify that the deviations were random. The correlation coefficient r (or $r^2$) provides a measure of the degree of variation for which the dependent variable can be accounted for by the model. The slope of the regression line describes the change in the dependent variable per unit increase of the independent variable. Ideally a one-to-one correspondence occurs. The intercept provides an indication of bias or systematic error present in the determination of the dependent variable and ideally should be zero in the absence of intrinsic influences.

For the data in Table 2, a high degree of correlation exists with $r^2 = 0.9987$. The slope is 0.9977 ± 0.0057 and is not significantly different ($P > 0.05$) from unity, indicating a one-to-one correspondence. The intercept value is -0.7621 ± 2.3879 and is not significantly different ($P > 0.05$) from zero, indicating the absence of any predominant systematic bias. A plot of the residuals against the predicted value (Fig. 1) revealed a fairly uniform pattern about zero. As anticipated, a greater absolute difference occurs between the larger concentration of $^{90}$Sr than between the smaller concentrations determined by the two methods, and such differences are exemplified in Fig. 1.

## SUMMARY AND CONCLUSIONS

The determination of $^{90}$Sr (via its $^{90}$Y daughter) by Cerenkov radiation counting on aqueous samples from monitoring wells within and near the solid low-level radioactive waste disposal areas at ORNL has been found to be highly correlated with standard chemical separations methodology. Comparisons of the two methods using paired concentration data were highly favorable and indicated no significant difference ($P > 0.05$). A considerable savings in time and expenses can be

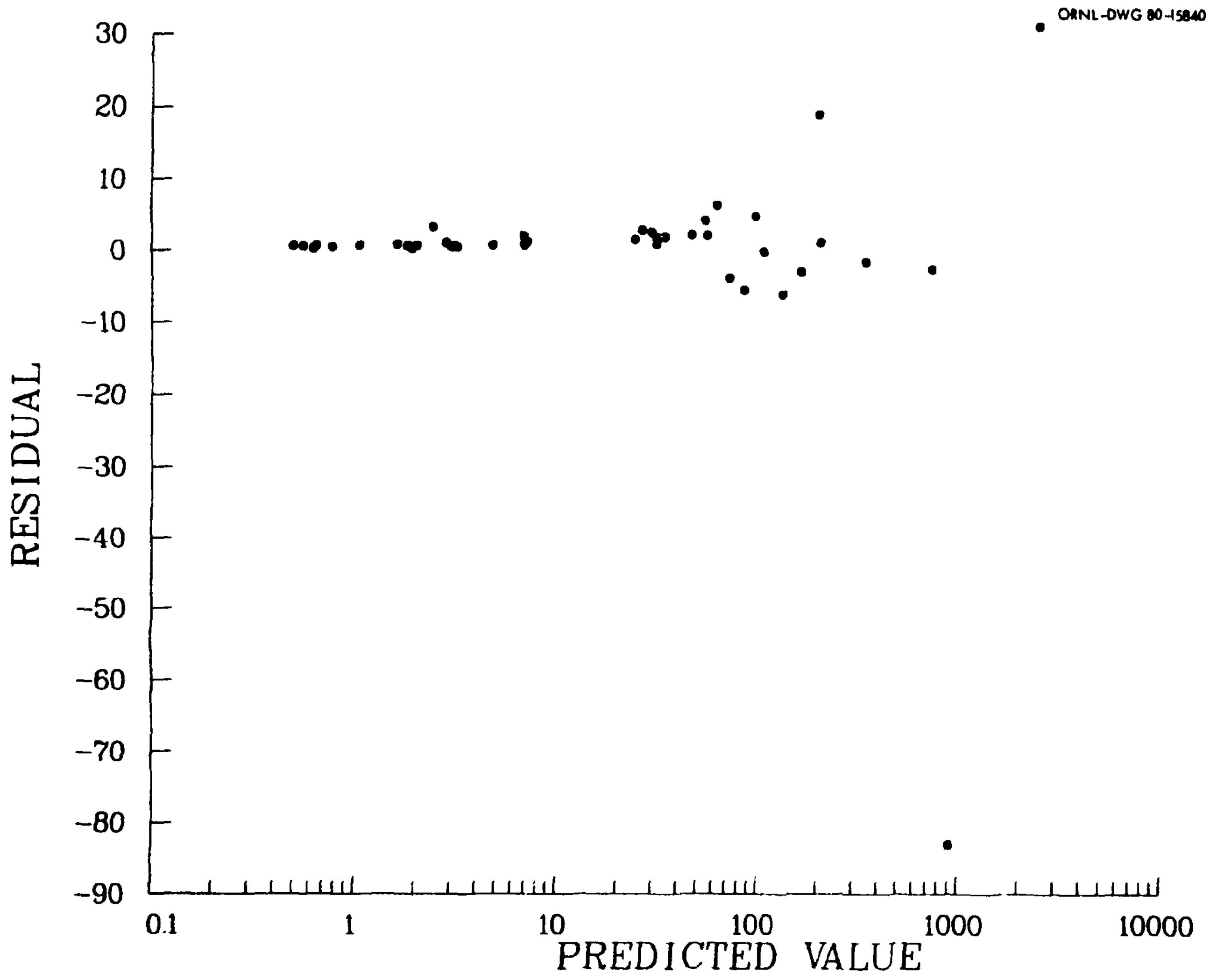

Fig. 1. A plot of the residuals (observed value minus predicted value) versus the predicted value for linear regression of Cerenkov radiation counting against analytical determinations. (For scaling purposes + 1 has been added to the predicted value along the abscissa.)

achieved by utilizing Cerenkov radiation counting to screen samples that contain little if any $^{90}Sr$ radioactivity. For example, the analysis of 119 monitoring well samples for $^{90}Sr$ concentrations by Cerenkov radiation counting revealed that only 33 samples (28%) contained $^{90}Sr$ concentrations of 3 pCi/mL (6.7 dpm/mL) or greater. These arbitrarily selected samples (33) were then submitted to the Analytical Chemistry Division for $^{90}Sr$ determination using standard wet chemical separation methods; this procedure eliminated from the tedious and costly analysis those samples that were low or near zero concentrations. Reductions (∿70%) in both cost and sample processing time were achieved by screening these samples by Cerenkov radiation counting.

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