This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-96SR18500 with the U. S. Department of Energy.

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A NEW APPROACH TO RADIONUCLIDE ANALYSIS IN GROUNDWATERS

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ABSTRACT

A method using liquid scintillation spectral analysis (LSSA) for analyzing mixtures of radionuclides in groundwater samples, which is fast, simple, and inexpensive, was developed and bench-tested. Samples can be measured in a field laboratory with a new commercial portable liquid scintillation instrument that provides advanced analysis, display, and computational features previously found only in large expensive laboratory models. Results can be available within hours from the time samples are collected. The analysis provides a good measure of total sample activity and a spectral index value that may detect changes in radionuclide distributions from previous analyses when counting statistic are adequate. If a sample shows no change, further analytical costs for it may be avoided.

A method that rapidly and quantitatively concentrates very low levels of activity from liter-size samples in minutes was also tested. With some modest improvements in this step, this work offers a completely new methodology and approach to groundwater remediation, which can dramatically reduce analytical costs and speed monitored cleanup and closure in many types of radiological work programs.

INTRODUCTION

Radiological contamination of some groundwaters is an unfortunate legacy of years of nuclear material production at a number of Department of Energy (DOE) research and production facilities. Among these is the Savannah River Site (SRS) near Aiken, South Carolina. Environmental remediation (ER) programs are in place to measure for groundwater contaminants and reduce them if necessary, but these programs by their nature may require years of treatment and measurements to monitor effectiveness and progress.

The measurement of low levels of radionuclides in groundwaters is difficult because they are sometimes present with much larger amounts of stable isotopes of the same or similar chemical identity. Differentiation usually requires lengthy and expensive chemical separations, which are a major expense in many current ER programs. At SRS, the target species of tritium, strontium, technetium, iodine, cesium, and uranium are of particular interest in ER programs. Analyses at typical environment levels for the first four species are practical only following chemical separation and beta counting, and for the sixth, by separation and alpha counting. Cesium often is determined by gamma counting and requires no separation. With each separation adding hundreds of dollars, total analysis costs for each sample are in the thousands of dollars. A large site like SRS may spend millions of dollars in analytical costs alone for ER and other closure programs.

Speeding analyses and reducing their cost in ER programs is an effective way to achieve accelerated cleanup at reduced expense sought by the DOE across its complex of nuclear sites.

AN ALTERNATIVE ANALYSIS METHOD

The most sensitive and inexpensive method for measuring beta and alpha activity in any liquid sample is by liquid scintillation counting (LSC). Furthermore, LSC is the only practical counting method for tritium that simultaneously offers very high counting efficiencies for all other alpha and beta emitting radionuclides. Traditional LSC alone, however, provides little or no information about the radionuclides responsible for the counts recorded. Instead it is used primarily to analyze samples containing only one or two known radionuclides, or when gross alpha or beta counts will suffice.

But simple LSC does not make use of the energy information that is inherent in the liquid scintillation process. The intensity of each light pulse produced by ionizing radiation from beta or alpha decay in a scintillation counting cocktail is proportional to the energy of the particle detected. All that is necessary to produce an energy spectrum of sample activity is to process the light pulses from the LSC’s photo-multiplier tube (PMT) through an analog to digital converter and store the digitized counts in a multi-channel analyzer (MCA). Packard Instrument Company, now owned by PerkinElmer, was one of the first commercial producers to offer this feature in their LSC instruments. Packard’s publication “Liquid Scintillation Analysis – Science and Technology” (1) presents an excellent treatise on the subject. Addition of an MCA adds a qualitative capability to LSC as well. With a spectral display of the decay energy of a sample, it is relatively easy to discern various types of nuclear materials responsible for the activity present if too many isotopes are not present. This is the basis of much of the low-level waste characterization methodology used at SRS. It was described and demonstrated nearly a decade ago by the first author of this paper in reference (2).

A major point made in reference (2) is that LSC captures the total radionuclide activity in a sample so there is rarely a need to identify every minor constituent in the mix, provided they are well known. The spectral shape, i.e. energy signature, identifies the genesis of nuclear material present, and prior detailed analyses and/or process knowledge is then used to quantify any constituent in the mix from established isotope ratio data. This is true at nuclear power plants and material production facilities, where fission yields and activation activity ratios are used to characterize most dry waste that is generated. Without such efficiencies in waste disposal many regulated industries throughout the world could not afford to operate.

An extension of this concept can be a basis for an alternative analysis method for groundwater samples. Since regulatory requirements for groundwaters are usually quite extensive, one and often multiple detailed analyses exist for all the historical samples previously collected. Repetitive samples are analyzed at some frequency in most ER programs to see if any significant change has taken place over a period of time. But if no change can be verified with adequate counting statistics, as is often the case, a detailed analysis of the sample provides no useful additional information. If this static condition can be shown by a more-simple alternative method, the delays and costs of many unnecessary laboratory analyses could be avoided. LSSA is such a method.

SPECTRAL INDEX OF THE SAMPLE AS A QUANTITATIVE VALUE

Reference (1) also describes the concept of the spectral index of the sample (SIS). The SIS is a numerical approximation of the center of gravity of a sample's beta energy expressed as:

$$\mathrm{SIS} = K \left[\sum_{x=0}^{u} x\, n(x)\right] / \left[\sum_{x=0}^{u} n(x)\right] \qquad \text{Equation 1}$$

where K is a normalization factor, x is the MCA channel number, n(x) is the number of counts in that channel, and u is the upper-channel limit of the spectrum. Mantel (3) in 1972 was able to calculate the average beta energy of some 59 isotopes from first principles and the Fermi theory of beta decay. The SIS value is shown in reference (1) to be directly proportional to the average beta energy as calculated by Mantel.

Just as the beta endpoint energy is an inherent property of a given isotope, so is its average energy and SIS value. However, unlike beta endpoint and average energy, SIS is not invariant. It is a measured quantity which decreases with increasing quench of a sample spectrum. The SIS value of a given isotope is often used as a quench-indicating parameter in LSSA in cases where counting statistics allow. Quench is a perpetual phenomenon in LSC applications that must be considered. This is best done by establishing a quench curve. The curve is determined by counting a fixed activity of a single isotope under optimal conditions (good counting statistics and corrected for background) with increasing amounts of a quench agent added to the fixed activity. Such curves turn out to be smooth parabolic functions of decreasing count rate with increasing quench. Using the known activity of the standards, the absolute counting efficiency versus quench-level is calculated. By also measuring the SIS value at each quench level, absolute counting efficiency, as a function of SIS, is mapped as well. A significant change in an unknown sample of a particular isotope can then be quantified by measuring its new SIS value and correcting it for counting efficiency from a previously established quench curve.

Intuitively, the functional form of the Equation 1 and the smooth continuous nature of quench curves indicate that an analogous approach ought to work for mixtures of different radionuclides as well. A mathematical proof may also be found in reference (1). We have confirmed this experimentally and the results will be described later in this paper. First, however, additional goals of this work and the experimental approach are discussed.

EXPERIMENTAL CONSIDERATIONS

Groundwater radionuclide contamination is typically quite small, on the order of picocuries or nanocuries per liter. The sample size for LSC is only a few milliliters at most, so preconcentration of the sample activity is a necessity. Laboratories usually rely on ion exchange methods to concentrate and separate the individual radionuclides. This works very well, but it is slow, demanding, and expensive. For some examples, the interested or unbelieving reader is referred to "LSC Handbook of Environmental Liquid Scintillation Spectrometry – A Compilation of Theory and Methods" (4). Consequently an additional aim of this study is to demonstrate a simpler and faster way to preconcentrate groundwaters so that analyses can be done onsite in a modest field laboratory. Ideally, results should be available within a day or two from the time the sample is submitted.

In theory, it should not be necessary to separate and measure the individual target radionuclides in recurring samples from a well that has been previously subjected to a full laboratory analysis. But, in practice, some separation is prudent. One of the SRS target nuclides is tritium. Tritium cannot easily be concentrated, and analysis is difficult unless most other activity is removed or is absent. Cation and anion species of the other target nuclides can be easily removed by ion exchange leaving a water fraction containing predominantly sample tritium. Similarly the target anions, Tc-99 and I-129, have much lower beta energies than the target cations, Sr/Y-90, Cs-137, and natural uranium. Unless the anions and cations are separated, small changes in the anion SIS values are difficult to verify in the presence of the much larger cation SIS values.

Lastly, the LSC instrument needs must be considered. A large machine is not needed. One that counts single samples manually is sufficient. Specifically, the LSC instrument must be able to count tritium and also samples with beta energies up to about 2000 keV. It must be able to display a sample spectrum and to do certain calculations on the data. Also, the ability to count and resolve alpha and beta activity is desirable, as is transportability. Until recently, some needed features could only be found in large expensive machines. But remarkably, now all of the desired features are available in an instrument 19-cm high, by 25-cm wide, by 33-cm deep and weighing 9 kg. It is the Triathler™ Multilabel Tester (5). It has a12-bit 700-ns ADC and digital signal processing. It counts beta energies from 2-2000 keV. The H-3 beta counting efficiency is > 20%, and it also can do alpha/beta discrimination. Disadvantages are primarily lower counting efficiency, lack of a quench correction source, and higher background than the large machines. In 2003, the Triathler™ costs about $15,000 with the alpha/beta discrimination option.

Recognizing the great potential for this instrument to open many new opportunities for field applications in ER, Solid Waste, and D&D work, SRNL purchased the instrument for evaluation and method development. When interfaced to a PC, the Triathler™ generates high quality spectral plots in linear or log format in seconds. Through its fast communications software and options available in Microsoft Windows™ Excel, SIS values can be calculated and shown on spectral plots as well.

EXPERIMENTAL RESULTS

NIST-traceable liquid standards for the six target radionuclides of interest in SRS ER programs were purchased from Analytics (6) in preparation for this work. These are shown in Table 1.

Table 1. Liquid Standards Purchased for this Study

Radionuclide	Quantity in Becquerels
H-3	3.956E+04
Sr-90	7.834E+04
Tc-99	3.873E+04
I-129	3.911E+03
Cs-137	3.891E+04
U-Nat	3.767E+02

The weighed standards were diluted to the volumes and activities listed in Table 2. The matrix-pH of each standard was maintained with the dilutions. The dilution volumes were set to give activities of >10,000 dpm/mL where possible. This was done to minimize the statistical uncertainties in count rates and to keep count times between 1-10 minutes for most tests. Several comments are necessary about Table 2. The actual activity for Sr-90 has been doubled to account for the Y-90 daughter, which is in secular equilibrium with the parent. The activity listed for Cs-137, when counted by liquid scintillation, is increased by about 10 % to account for the internal conversion electrons produced from the 662 keV gamma ray of Ba-137m. Also, the activity listed for natural uranium is just for the alpha decay. Thorium daughters are again in secular equilibrium and their beta activity doubles the rate if both alpha and beta are counted unresolved.

Table 2. Dilution Volumes and Activities of Prepared Standards

Radionuclide	ID# Date 10/7/03	Dilution Volume (mL)	Activity (dpm/mL)
H-3	SRS 67009-147	50	4.71E+04
Sr/Y-90	SRS 670010-147	100	4.66E+04
Tc-99	SRS 670011-147	50	4.61E+04
I-129	SRS 670012-147	50	4.65E+03
Cs-137	SRS 670013-147	50	4.63E+04
U Nat	SRS 670014-147	5	4.52E+03

The first experiments in the study were to measure the absolute counting efficiencies of the six target nuclides using the Triathler™. All of these measurements were made using polyethylene counting vials containing 19 mL of Ultima Gold™ AB (7) cocktail and 1 mL of the individual standards in Table 2. Blanks (cocktail only) were subtracted from all gross count-rate data. Results are shown in Table 3. The efficiencies listed for H-3 and U Nat are actually for different counting modes than the one used for the other four nuclides. The Triathler™ uses a different gain setting to optimize counting of H-3. The counting window was set for channels 20-130 instead of the factory value of 30-120, which is optimal for 7-mL counting vials. For the U Nat efficiency, the instrument was run in the resolved alpha-beta mode, which gives separate alpha and beta spectra. Special settings were optimized to obtain the best counting efficiencies and alpha-beta separation. These settings must be re-optimized for each different cocktail/vial combination used. The efficiency shown in the table is for total count rate in the alpha spectrum divided by the alpha dpm/mL rate in Table 2. The other four nuclides were counted in the instrument's P-32 mode that sets the gain for a 2-2000 keV energy spectrum.

Table 3. Absolute Counting Efficiencies Measured with Triathler™

Radionuclide	Counting Efficiency (%)
H-3	27.2
Sr/Y-90	95.2
Tc-99	85.8
I-129	66.3
Cs-137	96.6
U Nat	78.8

Quench Curve Development

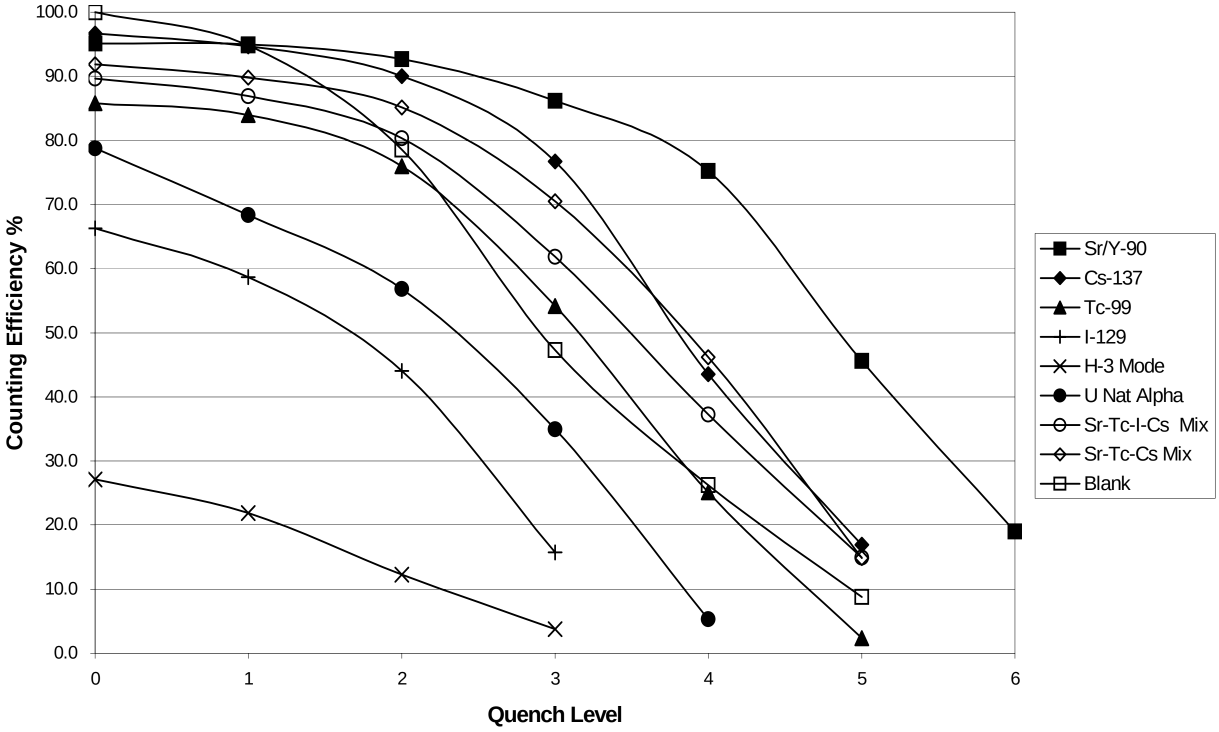
The Triathler™ boasts a feature that the vendor clams is very helpful in developing quench curves. Instead of making duplicate standards and adding different amounts of a quench agent to each, the Triathler™ allows the cap of its counting chamber to be partially opened as a way to mimic the loss of light that occurs when a sample is quenched. Furthermore, if the user marks the cap and instrument chassis with lines indicating the rotation of the cap away from fully closed, the level of quench for any nuclide can be reproducibly varied over a desired span. We used the approach to generate quench curves, but we did not attempt to validate it against the traditional quench-set method. Seven quench lines were marked nearly evenly on the chassis to mimic zero quench to high quench.

The Triathler™ has a single PMT and thus is not as efficient as large laboratory machines that have better optical coupling characteristics and two PMTs. The effect is most evident for the low energy beta emitters H-3 and I-129. Still the efficiencies are quite respectable and usually far surpass those achievable with other counting technologies. (The counting efficiency for tritium reportedly is 42% if 7-mL counting vials are used.)

Quench Curve Generation

The six standards were counted at each quench level. Gross blank counts at the same levels of quench were subtracted from each standard count. Separate blank and standard quenches were measured for the P-32, tritium, and alpha counting modes. Net count rates and SIS values were calculated for each standard and quench level. The individual data are of little importance and apply only to this instrument and its particular settings. Rather quench curves spanning a working range for each standard are what is pertinent, and these are presented in Figure 1. Quench level zero indicates the standard counted as prepared with no additional quench. Six is the highest level of quench considered as it was sufficient to reduce the counting efficiency to 20 % or less of the unquenched count. It is seen that the level of quench which reduces the counting efficiency by this amount depends on the endpoint energy of each target nuclide. The highest in the P-32 mode is Sr/Y-90 with an endpoint energy of 2280 keV. The lowest is I-129 at 194 keV. The special counting modes for tritium and alpha cannot be compared directly to the P-32 mode. But it is clear that tritium with an endpoint energy of 18.6 keV can tolerate very little quench.

Figure 1. Absolute Counting Efficiency vs Quench

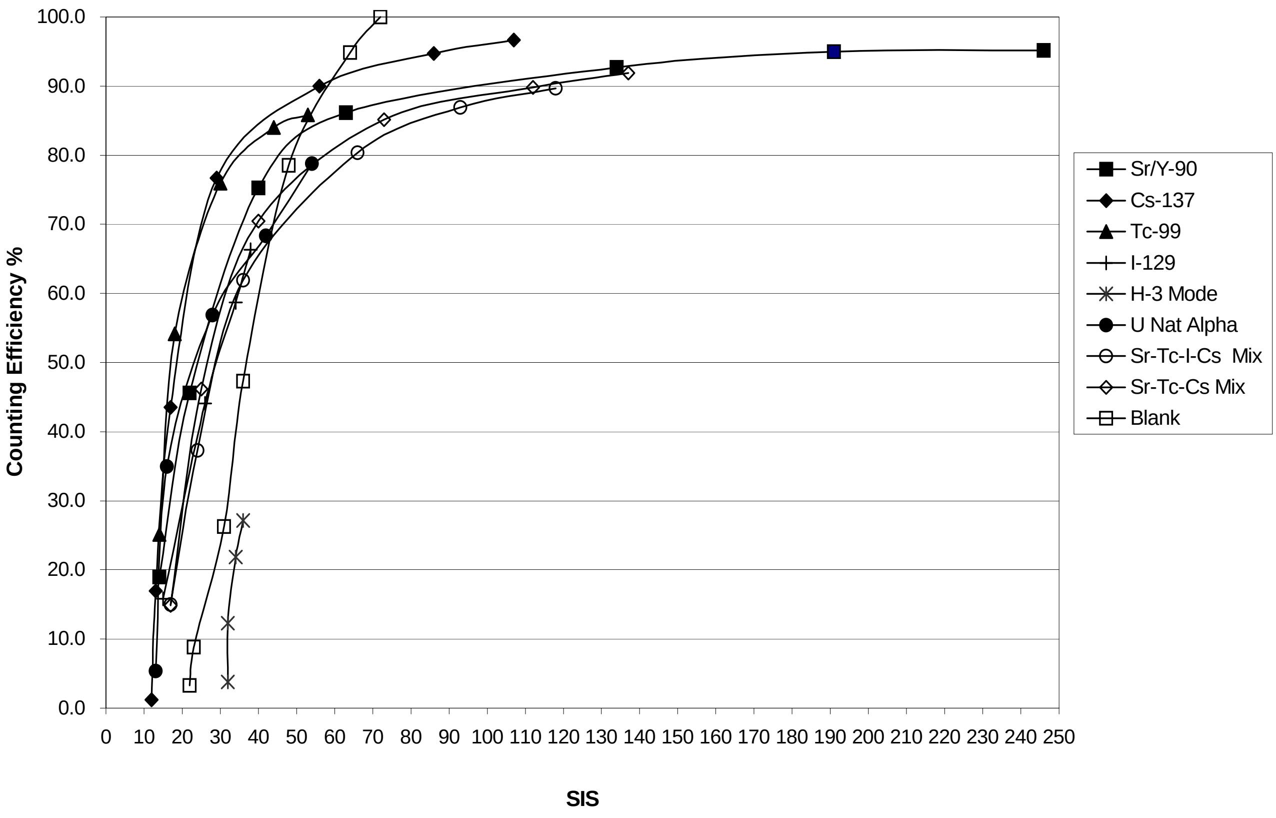


All the curves exhibit similar parabolic shapes characterized by slight losses in efficiency at low quench levels leading to a knee in the curve. Beyond the knee the loss in efficiency is much more rapid with increasing quench. Some of the differences at the higher quench levels may be due to statistical uncertainty caused by the blank subtractions from the low gross count rates. Two mixed standards are included, and their shapes are similar to those of the individual components in the mix. Finally, the quench curve for the blank is seen to have a somewhat different shape. It falls more sharply at low quench and appears to bend back at higher quench. This may be understood from the fact that counts in the blank arise primarily from gamma radiation and cosmic background events external to the vial but interacting with the scintillation cocktail inside the vial. It is dominated by many low-energy events that fall off rapidly with quench; at higher energies, the spectrum is flat, nearly constant, and changes little with quench.

SIS Value as a Measure of Quench

Figure 1 is instructive in that it shows that the effect of quench on counting efficiency is a smooth continuous function as expected. Otherwise it is of little use because quench level is but a numberless qualitative adjective, and there is no way to predict what it is in an unknown sample. This problem disappears if a sample's SIS value is measured. This may be seen in Figure 2 which

Figure 2. Absolute Counting Efficiency vs SIS



is a plot of counting efficiency vs. SIS. The points on each curve mark the measured SIS value and counting efficiency at the different quench levels. Here the similarity in curves is even more striking than in Figure1. They almost all lay on top of one another, except for differences in maximum counting efficiency and knee location. Every curve has a different SIS value at a particular level of quench. The SIS value also is a measure of the center of gravity of the beta energy spectrum, so the higher the SIS value the higher the average and beta endpoint energy of a constituent. The curves for tritium, U Nat, and the blank are different from the others in the figure. The reasons for this were mentioned above. In addition, the uranium standard, as prepared, suffers color and chemical quench due to its concentration and matrix. This is evident in the abnormally small initial SIS value. Also, the blank is not the result of beta decay, so its contribution to the SIS of a sample is not easy to remove. This has significance to further discussions of the data in the next section.

Other Useful Aspects of the SIS Value

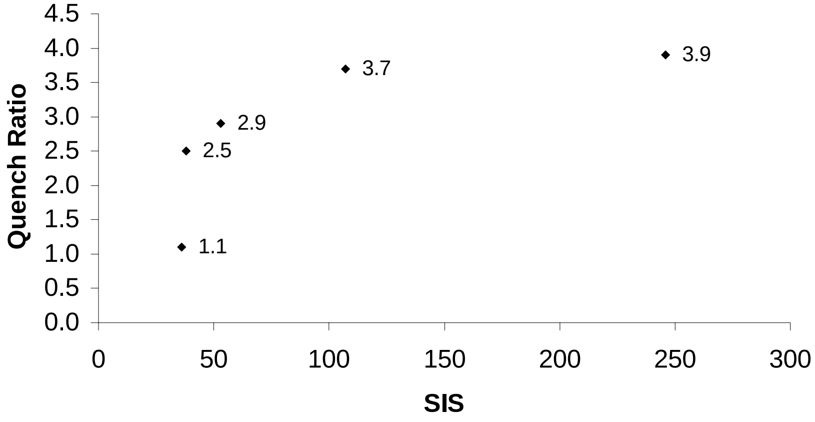
The changes in SIS with quench in a particular sample exhibit additional qualitative information about its constituents. Consider Table 4 which shows numerically how the same levels of quench affect the SIS values of different types of radioactive decay.

Table 4. Quench Effects on SIS Change for Different Sample Types

Radionuclide	SIS-0	SIS-3	Decay	End Point (keV)	Quench Ratio
Sr/Y-90	246	63	β	546 + 2280	3.9
Cs-137	107	29	β + IC	512 + 630	3.7
U Nat	54	16	α	≈ (500)	3.4
Tc-99	53	18	β	294	2.9
I-129	38	15	β	152	2.5
Blank	72	36	Cosmic	None	2.0
H-3	36	32	β	18.6	1.1

This is best seen over a large level of quench. The SIS values at quench levels zero and three are used to illustrate, and the ratios of the two are shown in the last column in descending order. The different types of radiation responsible for the scintillation spectra are shown in the decay column. The end-point column lists the maximum beta equivalent energy of each unquenched spectrum. Except for uranium and the blank, the ratios appear to decrease proportionally with the unquenched SIS value of each sample. The anomalous behavior for uranium (SIS-0=54) and the blank (SIS-0=72) as noted earlier are due to their decay modes compared to the others in the table. The blank spectrum is the result of mostly cosmic events. These extend to very high energies and have no defined end point. Natural uranium decays by alpha emission and is nearly mono-energetic compared to beta decay. The result is a peak in the spectrum which should have an apparent energy of approximately 500 keV on a beta energy scale. Its SIS-0 value is instead almost the same as that of Tc-99's 294 keV endpoint. Because SIS is proportional to average beta energy which is about one-third the endpoint energy, an SIS of 53 is equivalent to only about 100 keV. This large discrepancy is caused by the large chemical and color quench of the natural uranium standard mentioned above. A less noticeable anomaly occurs with Cs-137. Its is caused by internal conversion electrons produced from the Ba-137m gamma rays that are in secular equilibrium with the Cs-137 beta decay. These conversion electrons are essentially mono-energetic at about 630 keV. The fixed, high energy of conversion electrons are affected less by small amounts of quench than the extended lower energy signature characteristic of pure beta decay. Also, Cs-137 has a second beta branch of about 5% probability at 1170 keV. Both factors cause the quench ratio of Cs-137 to be slightly high comparatively in Figure 3. Figure 3 looks much like the curves of the pure beta-emitters (Sr/Y-90, Tc-99, I-129 and also H-3 whose SIS is somewhat high relative to the others because of the special tritium counting mode used by the Triathler™) in Figure 2. This is but further proof of the fact that liquid scintillation counting efficiency decreases with increasing quench. Since SIS is directly proportional to the average energy of the observed spectrum and indirectly to the actual energy spectrum, so too must counting efficiency decrease as the overall constituent energies decrease.

Figure 3. Quench Ratio Effects on SIS



Cumulative Properties of SIS Values in Mixtures

Because the SIS value is a measure of the center of gravity of a sample's energy spectrum, it follows that the SIS of a mixed sample can be predicted from the activity-weighted sum of the SIS values of its individual components. For instance, the SIS of a mixture of equal activities of two different radionuclides should equal the sum of their individual SIS values. This was tested by preparing five different standard mixtures and measuring their SIS values. The data are shown in Table 5. Five mixtures were prepared by pipetting between 0.75 and 1.75 mL of the various standards into 19 mL of liquid scintillation cocktail. SIS values for each were calculated by summing the activity fraction (AF) of each standard multiplied by its pure SIS value. The last column in the table gives the ratio of the measured to the calculated SIS values. Agreement is excellent.

Table 5. Comparison of Measured and Calculated SIS Values for Mixed Standards

Nuclide	Sr/Y-90	Cs-137	Tc-99	I-129	SIS (Meas.)	SIS (Calc.)	Ratio
Volume (mL)	0.50	0.50					
Activity (dpm)	2.35E+04	2.57E+04					
SIS x AF	246 x 0.478	107 x 0.522			170	173	0.98
Volume (mL)	0.25	1.00					
Activity (dpm)	1.18E+04	5.14E+04					
SIS x AF	246 x 0.187	107 x 0.813			127	133	0.95
Volume (mL)	0.10	1.00					
Activity (dpm)	4.70E+03	5.14E+04					
SIS x AF	246 x 0.084	107 x 0.916			117	119	0.98
Volume (mL)	0.25	0.25	0.25				
Activity (dpm)	1.18E+04	1.28E+04	1.16E+04				
SIS x AF	246 x 0.326	107 x 0.354	53 x 0.320		140	135	1.04
Volume (mL)	0.25	0.25	0.25	1.00			
Activity (dpm)	1.18E+04	1.28E+04	1.16E+04	9.39E+03			
SIS x AF	246 x 0.259	107 x 0.281	53 x 0.254	38 x 0.206	119	115	1.03

Since the total is the sum of the parts, one might reasonably ask if it is necessary to measure each part to see a difference in the sum. Actually, as a test for statistically significant change, measuring the sum of the radionuclides is usually better than measuring the individual components. Each analytical measurement inherently involves uncertainty. For instance if a sample contains say five radionuclides each at 0.37 Bq, its total activity would be 1.85 Bq or 111 dpm. Assuming zero background, an overall counting efficiency of 50%, and a one-hour long measurement, the total counts recorded should be 3330 ± 3.5 % at the 95% confidence level. On the other hand if each individual component is separated and then counted under the same conditions, each count would give a result of about 666 ± 7.7%. The sum of the five counts would still be 3330, but the 95% confidence level rises to 17.2 % because the individual uncertainties sum in quadrature. To obtain the same counting precision as the single total measurement, the five components would each need to be counted for about 24 hours. A laboratory with a single LSC would require five days of counting, not to mention the time and cost for separating the five species from the original sample. Too, each separation would add in additional uncertainty of at least several more percent. The end result would likely have a total uncertainty of at least 10%.

Despite the additional cost in time and money, results by component analysis are invariably less certain than the result from a single gross count. One might argue that one component could drop by the same amount that another rose and go unnoticed. But the total SIS value would likely change, because individual SISs of the varying components are unlikely to be equal.

In principle, the SIS value of any mixture of radionuclides can be calculated provided the activity fractions and the SIS values of the individual components are known. SIS is dependent only upon beta energy and quench. Therefore if the sample SIS changes, either its composition, quench, or both must also have changed. If a sample contains but a single radionuclide, nothing but a change in quench will affect the SIS value. Since quench in groundwaters is affected almost entirely by the chemical composition of a sample as opposed to its radiological composition, SIS is also a unique and very sensitive indicator of changes in the chemical composition of almost any sample. Chemical composition changes in samples containing little or no radioactivity also can be tested by a standard addition of an appropriate innocuous radionuclide. This also applies to establishing the quench in low activity samples.

Extraction Disk Tests Results

Groundwater analyses typically pose another problem: very low levels of radionuclides. The analysis of an assumed 1.85-Bq sample above is near the norm for ionic radionuclides per liter of contaminated SRS groundwaters, although tritium is typically much higher. But this is the level in a one-liter sample. So, the radionuclides in groundwater samples require concentration before they can be analyzed. The standard practice is to use appropriate ion exchange methods to both concentrate and separate the radionuclides from one or a few liters of the groundwater. While concentration is mandatory, complete separation of the individual species is not if LSSA is used instead of simple LSC.

Because LSSA does not require complete separation of sample radionuclides, direct counting of ion exchange resins seemed like a possible way to bypass the lengthy and complex laboratory process of eluting and counting each nuclide separately. Using a cation and an anion resin sequentially is particularly attractive because it eliminates potential masking of small SIS changes of low-energy anion betas by the high-energy cation betas in the counting steps. Attempts to do this, however, were unsuccessful. Both types of resin (8) failed to form stable suspensions when mixed with Ultima Gold™ AB cocktail. Addition of a thixotropic agent, Cabosil (9), to the cocktail did not work either. Both resins also noticeably colored and quenched the cocktail.

Rather than devote more effort to solving the ion exchange resin approach, a newer technology, 3M™ Empore™ Extraction Disks (10), was tried. An attractive feature of extraction disks is that they can concentrate ions very fast compared to resin methods. Anion or cations in a liter of water can be extracted in less than ten minutes. The disks are 47 mm in diameter and just fit into a 20-mL LSC vial. Their extraction capacity is only about 0.4 milliequivalents per disk, so they are only suitable for fairly clean waters. Most groundwaters at SRS qualify. Calcium in some samples might occasionally exceed the disk capacity at up to about two-meq/L (11). But the calcium content of water is easily checked in the field, so water volume can be adjusted accordingly. Another concern is with the counting efficiency of a disk when placed in a liquid scintillation vial. Due to their size, they eclipse part of the light path to the single Triathler™ PMT. Also, unlike the anion disk which is bright white, the cation disk is tan in color and adds further quench to the scintillation cocktail.

A series of quick experiments were performed to see if the target cations and anions can be concentrated onto extraction disks and then counted directly by liquid scintillation. To partially simulate the dilute condition of groundwaters, standards were made up to nominally 100 mL and vacuum extracted using self-contained Nalgene™ filter units with either a cation or anion extraction disk substituted for the normal filter paper. Because recoveries, counting efficiencies, and quench effects for these disks were unknown, a Packard laboratory model LSC unit was used for all measurements in these tests. This instrument offers better counting efficiency, lower background, and more extensive capabilities than the Triathler™. Only the four ionic beta-emitting nuclides (Sr/Y-90, Tc-99, I-129, and Cs-137) were tested. Uranium was not included because its alpha/beta emission will likely require further optimization studies for field application as discussed in the next section.

Counting results and pertinent conditional parameters for the experiments are shown in Table 6. The first column of the table lists the individual radionuclides or mixtures tested. The second column shows the nominal pH values of each 100-mL standard used. This is an important parameter because it affects the practical extraction efficiency of the disks. Instructions for using the disks suggest that pH be two units below the pK_a values of the species to be extracted. This is particularly true for the multi-valent ions of iodine and possibly technetium. TSIE in column three is a quench-indicating parameter that Packard uses in its high-end LSCs. Like SIS, quench varies inversely with TSIE. Note that in cation experiments, TSIE is low due to the tan color of the disk; the anion disk is white and has much higher TSIE values. The next two columns show the counts on the disks and in the filtrates respectively. From the added activities in the sixth column, recoveries and counting efficiencies were calculated.

Table 6. Results and Conditions for Extraction Disk Experiments

Label	pH	TSIE	Disk (cpm)	Filtrate (cpm)	Activity (dpm)	Recovery (%)	Efficiency (%)
Cs-137	3.6	196	7115	<650	1.14E+04	>92	68
Sr/Y-90	3.6	178	9890	<650	1.15E+04	>94	92
I-129	10.3	400	5800	1870	9.3E+03	76	82
I-129	7.0	429	7720	<720	9.3E+03	>91	91
I-129	5.0	434	6660	<720	9.3E+03	>90	79
I-129	5.0	518	3000	4230	9.3E+03	41	78
Tc-99	8.4	420	4580	5220	1.15E+04	47	85
Tc-99	6.0	432	3785	5570	1.15E+04	40	81
Tc-99	6.0	548	8160	3440	1.15E+04	70	101
Tc/I	5.0	479	18600	<720	2.08E+04	>96	93
Cs/Sr	3.3	194	11390	2280	2.29E+04	83	60
Cs/Sr/I/Tc	3.5	177	14490	22300	4.37E+04	39	84

For each experiment there are data for two counts. The first lists the cpm activity captured on the extraction disk. The other is the total filtrate cpm activity based on a 2-mL aliquot count. The recovery values are calculated by dividing disk cpm values by the sum of the disk and filtrate values. Counting efficiencies in the last column are expressed as the sum of the disk and filtrate counts divided by the activity dpm values. Counting efficiencies in all but two cases are about 80% or greater. This is a reflection of the Packard's design. The exceptions are both for cases involving Cs-137. This is likely due to the color quenching of the cation disk and the lower average beta energy of Cs-137 compared to Sr/Y-90. Cs-137 is the least important target nuclide in groundwater remediation studies at SRS because it occurrence in site groundwaters is often too low to measure. Also it can usually be measured by gamma counting if necessary.

The variations in recoveries can be understood largely from the pH data shown for the different experiments. All the experiments that show less-than values in the filtrate have high computed recoveries. As true filtrate activities could be much lower than the less-thans, actual recoveries may be closer to 100%. Results of the first two experiments compared to the last two indicate that complete recovery of the cations is not favored when pH is less than about 3.6. For the next to the last experiment, some activity clearly passed through the disk and into the filtrate, and in the last experiment the 22,300 counts found in the filtrate exceeds the anion activity that should have passed through the disk. This may be caused by displacement of Cs-ions from the disk by H_3O^+ ions.

The four I-129 experiments also show significant pH effects. In the first one at pH 10.3, iodine should have been present primarily as IO_3^-. The mediocre collection efficiency suggests that iodate ions are not retained particularly well on the anion extraction disk at this high pH. At the lower pHs of the next two experiments, most iodine is present as I^- and is retained on the disk quite well. For the last I-129 experiment at pH 5, the starting solution was reduced with 4 mL of 1.0M sodium sulfite. The intent of this was to insure all the iodine was present as iodide. In retrospect this was a mistake. The sulfite addition exceeded the capacity of the extraction disk, and much of the iodide that should have been retained on the disk was likely displaced by divalent sulfite instead.

Finally in the Tc-99 experiments, pH effects are less apparent. In the first two with pHs of 8.3 and 6.0, recoveries were rather poor at 47% and 40% respectively. Both cases showed more activity in the filtrate than on the disk. The third experiment also at pH 6 showed some improvement with 70% recovery. This solution was also reduced with sodium sulfite in an attempt to favor pertechnetate formation. This may have worked, but again sulfite likely displaced some TcO_4^-. The mixed Tc/I experiment however shows that at a lower pH of 5.0, full recovery apparently was obtained for both technetium and iodine. Technetium likely can be completely recovered at a pH of 5.0 without any further chemical adjustment

Considering all the data, it appears that all the cations and anion can be completely extracted at pH 4-5 provided the ionic strengths in groundwaters of interest do not exceed the capacity of the extraction disks. Another caveat is that for fieldwork, the Triathler™ is the instrument of choice for counting measurements. The Triathler™'s single PMT and the higher background in contrast to large laboratory models translates into lower counting efficiencies. These were determined by counting the extraction disks in Table 6 with the highest recoveries with the Triathler™. Counting efficiencies were reduced to about 25% for Cs, 50% for Sr/Y, 60% for Tc, and 45% for I. Though lower, the numbers are still quite acceptable under the considerations mentioned in the next section.

PRACTICAL LSSA CONSIDERATIONS FOR GROUNDWATER REMEDIATION WORK

For LSSA to be a viable method in groundwater remediation work, there must be sufficient detectable radioactivity activity present in perspective samples. Detection limits are often listed for a method as the minimum amount of activity that must be present to be detected with reasonable certainty. However for data to be quantitative with a good precision and accuracy, activity levels need to be at least several times higher than the detection limit. When groundwater is found to have radiological contamination, remediation is usually required if levels exceed the Derived Concentration Guides (DCG) established in U.S. Department of Energy Order 5400.5, “Radiation Protection of the Public and the Environment”. DCGs for the six SRS target radionuclides are listed in Table 7 along with the estimated minimum detection limits (MDLs) achievable by this method. The MDLs are based on the laboratory tests discussed above. Actual MDLs remain to be established by field studies at some future time.

Being able to verify that the maximum activity in a sample is below the most restrictive applicable regulatory limit in question is the key to a method’s suitability for routine monitoring because complete speciation is then unnecessary. More detailed analyses are only needed when simple monitoring cannot verify this critical regulatory limit. Occasionally complete speciation may be important for other reasons, but minimizing these is essential to cutting analytical costs.

The most restrictive DCG are groundwaters are for Sr-90, I-129, and natural uranium. LSSA for uranium is not practical using extraction disk concentration as alpha-beta resolution is lost with the high quench introduced by the disk. The Triathler™’s vendor claims a method based on a simple liquid-liquid extraction of aqueous uranium into certain organic scintillation cocktails has achieved a detection limit of about 0.04 Bq /L for a 30 minute counting time.

Table 7. Estimated MDLs Versus DCGs for SRS Target Radionuclides

Radionuclide	DCG (Bq/L)	Estimated MDL (Bq/L)
H-3	74000	2400
Sr-90	37	0.8
Tc-99	3700	0.5
I-129	18.5	0.7
Cs-137	111	0.7
Natural Uranium	22.2	0.04 (Vendor’s Claim)

This very low MDL suggests such an extractive procedure could be used to pre-extract uranium from a groundwater sample prior to preconcentration by the extraction disks. Our laboratory estimated MLDs are well below the applicable DCGs. The most restrictive is 0.7 Bq/L for I-129 which is a factor of nearly 25 times lower than necessary to demonstrate compliance. So, LSSA as outlined above would appear to be a viable alternative method worthy of field-testing.

CONCLUSION

A conundrum exists in radionuclide analyses performed under regulatory program guidelines. Laborious and lengthy analyses are often prescribed for reasons that have little to do with data quality needs. Instead requirements are driven largely by legal considerations in the event of litigation in the courts. This is well and good as long as the costs are affordable. But, as the DOE and other custodians of lands with radiological contamination are discovering, budgets cannot sustain such levels of efforts indefinitely.

Groundwater remediation is just such a program. When groundwater is found to have radiological contamination, remediation is usually required. Most remediation schemes take months or years to see significant improvements in water quality. With prescribed analysis requirements often running several thousands of dollars per sample, the long-term cost of monitoring the many remediation wells may exceed those of the treatment. Reducing the cost of analyses in these projects surely would significantly lower projected expenditures for cleanup.

Advances in the capabilities of field-portable nuclear counting instrumentation continue to make possible analyses that previously could only be done in the laboratory. This is particularly true of liquid scintillation counters. The Triathler™ Multilable Tester evaluated in this study is one such. With it, many types of radiation measurement or monitoring applications can be conducted more quickly, conveniently, and cheaply than ever before. The combination of LSC’s high counting efficiency for any and all radionuclides and simplicity of use could be the answer to accelerated cleanup at reduced cost for many radiological tasks. Groundwater remediation programs are ideal candidates because the analysis matrix is the relatively clean and easy to work with, but many other applications are also imaginable.

The problems of simple LSC are chiefly sample preparation, quench, and the perception that it cannot provide the level of qualitative information necessary if mixtures of radionuclides are involved. These have been overcome in the laboratory, and this study has reexamined all three problems and shown that LSSA can largely solve them for groundwaters. This can be done in the field with recourse to only modest laboratory facilities.

The sample preparation problem is one of concentrating the radionuclides from a large dilute matrix into a few milliliters inside an LSC counting vial. Ion exchange has been the solution and still is. But for many groundwaters, beta emitting anions and cations can be collected on separate extraction disks and placed directly into the scintillation cocktail for counting. Analysis then consists of counting an aliquot of the filtrate water, which contains primarily tritium, and the anion and cation disks. This can all be done onsite in a matter of hours. A separate but simple procedure seems promising for direct LSSA application to actinides in groundwaters as well.

Although quench is a perpetual problem with LSC, the Triathler™ appears to make the preparation of quench curves for any sample media quick and easy. PC software interfaced to the Triathler™ can compute quench and produce a spectral plot in seconds. With the spectrum in a PC, more sophisticated and complicated analysis options are available to meet more challenging demands. Sample quenching becomes quantitative and partly qualitative through the measure of SIS. The energy spectrum contains all the information necessary to confirm the sample's radionuclide composition and total activity. Many groundwaters change little or not at all in the course of remediation. If this is confirmed simply in quick field measurements, costly follow-up laboratory analyses are mostly unnecessary.

The perception that LSC is unsuitable for analyzing mixtures of radionuclides is true only if the energy spectrum of the sample is absent or cannot be viewed. With the Triathler™, one is always available. It can be used as a visual record for comparisons, or under a trained eye, it can provide much qualitative information. The same measured unique SIS parameter that relates to quench also relates to energy of the sample's spectrum. Two samples with the same SIS values and spectral shapes have identical compositions. If so, total activity is the only important variable and the essential measure of progress in remediation.

Previous perceptions by regulators will persist until the analytical community presents demonstrative data to prove that there is a cheaper, faster, yet valid way to proceed with regulatory radiological work. Shrinking budgets suggest this is the time to start the process.

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