EPA/600/R-11/181
www.epa.gov/narel
November 2011
Revision 0

Rapid Radiochemical Method for Phosphorus-32 in Water for Environmental Remediation Following Homeland Security Events

U.S. Environmental Protection Agency

Office of Air and Radiation
Office of Radiation and Indoor Air
National Air and Radiation Environmental Laboratory
Montgomery, AL 36115

Office of Research and Development
National Homeland Security Research Center
Cincinnati, OH 45268

Revision History

Revision 0	Original release.	11/17/2011

This report was prepared for the National Air and Radiation Environmental Laboratory of the Office of Radiation and Indoor Air and the National Homeland Security Research Center of the Office of Research and Development, United States Environmental Protection Agency. It was prepared by Environmental Management Support, Inc., of Silver Spring, Maryland, under contract EP-W-07-037, work assignment I-41, managed by David Garman and Dan Askren. Mention of trade names or specific applications does not imply endorsement or acceptance by EPA.

Rapid Radiochemical Method for Phosphorus-32 in Water for Environmental Remediation Following Homeland Security Events

1. Scope and Application
   1.1. The method will be applicable to water samples where radioactive contamination is either from known or unknown origins. If any filtration of the sample is performed prior to starting the analysis, those solids should be analyzed separately. The results from the analysis of these solids should be reported separately (as a suspended activity concentration for the water volume filtered), but identified with the filtrate results.
   1.2. The method is specific for ^{32}P in drinking water and other aqueous samples. ^{33}P, another long-lived isotope of phosphorous, may be present in the sample. However, since the beta particle energy is insufficient to generate Čerenkov radiation, it will not interfere with analysis for ^{32}P by this method.
   1.3. The method uses rapid radiochemical separation techniques for determining ^{32}P in water samples following a radiological or nuclear incident. Although the method can detect concentrations of ^{32}P on the same order of magnitude as methods used for the measurement of gross beta concentration for the Safe Drinking Water Act (SDWA), the method cannot be used for SDWA applications because no ^{32}P-specific method has been approved by EPA.
   1.4. The method is capable of achieving a relative required method uncertainty for ^{32}P of 13% at an analytical action level (corresponding to a 100-mrem dose rate for 50 years) of 12,000 pCi/L with 100 mL of sample and a counting time less than 30 minutes (see Steps 9.2 and 9.3). A larger sample size, followed by concentration and purification of phosphate, and a longer counting time is necessary to achieve a comparable SDWA detection level for gross beta concentration of 3 pCi/L (see Step 9.4). The Safe Drinking Water Act Maximum Contaminant Level (MCL) for ^{32}P is 30 pCi/L.
   1.5. The sample turnaround time and throughput may vary based on additional project MQOs, the time for analysis of the final sample test source, and initial sample volume. The method must be validated prior to use following the protocols provided in *Method Validation Guide for Qualifying Methods Used by Radiological Laboratories Participating in Incident Response Activities* (See Reference 16.1).
   1.6. The method is intended to be used for water samples that are similar in composition to drinking water or surface water. The rapid ^{32}P method was evaluated following the guidance presented for "Level E Method Validation: Adapted or Newly Developed Methods, Including Rapid Methods" in *Method Validation Guide for Qualifying Methods Used by Radiological Laboratories Participating in Incident Response Activities* (see Reference 16.1) and Chapter 6 of *Multi-Agency Radiological Laboratory Analytical Protocols Manual* (MARLAP 2004, Reference 16.2). The matrix used for the determination of ^{32}P was drinking water from Atlanta, GA.
   1.7. The method is applicable to the determination of soluble ^{32}P. The method is not applicable to the determination of ^{32}P in highly insoluble particulate matter possibly present in water samples contaminated as a result of a radiological dispersion device (RDD) event. The source of such materials may be brachytherapy sources encased in a Ti-Ni casing. The proprietary nature of the chemical form of these sources makes it difficult to establish a chemical analysis method. Suffice it to say that the acid digestion

steps used in this method would be insufficient to dissolve such sources. This also means that they would not be available for intake and accumulation in the body. For this reason, the water sample is filtered first. The filtered residue should be retained for subsequent analysis.

2. Summary of Method
   2.1. A 100 mL water sample is filtered and phosphate carrier is added. The solution is passed through a cation exchange resin and then a Diphonix® resin to remove interferences from cation radionuclides. The eluent is treated with a mixture of 10 mL of 30 % H_2O_2 and 10 mL of concentrated nitric acid, reduced in volume, by heating, to approximately 2 to 5 mL, and quantitatively transferred to a LSC vial for counting. The Čerenkov photons from the ^{32}P beta (1710 keV, E_{max}) decay are detected using a calibrated liquid scintillation counter (LSC). Following counting of the sample, an aliquant of the final solution is used for yield determination by the inductively coupled plasma-atomic emission spectrometry (ICP-AES) method.

3. Definitions, Abbreviations, and Acronyms
   3.1. Analytical Protocol Specifications (APS). The output of a directed planning process that contains the project's analytical data needs and requirements in an organized, concise form.
   3.2. Analytical Action Level (AAL). The term "analytical action level" is used to denote the value of a quantity that will cause the decisionmaker to choose one of the alternative actions.
   3.3. Analytical Decision Level (ADL). The analytical decision level refers to the value that is less than the AAL and is based on the acceptable error rate and the required method uncertainty.
   3.4. Discrete Radioactive Particles (DRPs or Hot Particles). Particulate matter in a sample of any matrix where a high concentration of radioactive material is contained in a tiny particle (diameter is in the micro-meter range).
   3.5. Figure of Merit (FOM). The figure of merit is a measure of the response to the analyte by the instrument relative to the background. The FOM is the square of the detector efficiency divided by the background count rate, both measured in the same region of the spectrum.
   3.6. Liquid Scintillation Counter or Counting (LSC). A beta spectrometer used to measure Čerenkov radiations.
   3.7. *Multi-Agency Radiological Laboratory Analytical Protocols Manual* (see Reference 16.2).
   3.8. Measurement Quality Objective (MQO). MQOs are the analytical data requirements of the data quality objectives and are either project or program specific. They can be quantitative or qualitative. MQOs serve as measurement performance criteria or objectives of the analytical process.
   3.9. Radiological Dispersal Device (RDD), i.e., a "dirty bomb." This is an unconventional weapon constructed to distribute radioactive material(s) into the environment either by incorporating them into a conventional bomb or by using sprays, canisters, or manual dispersal.

3.10. Region of interest (ROI). The region of interest is that part of the spectrum for a particular analyte or group of analytes where it is expected that the instrument will have the most analytically favorable response. The ROI is user selected, often by using the FOM calculation for different regions of the spectrum.

3.11. Required Method Uncertainty (u_{MR}). The required method uncertainty is a target value for the individual measurement uncertainties and is an estimate of uncertainty (of measurement) before the sample is actually measured. The required method uncertainty is applicable at or below an AAL.

3.12. Required Relative Method Uncertainty (φ_{MR}). The required relative method uncertainty is the u_{MR} divided by the AAL and typically expressed as a percentage. It is applicable above the AAL.

3.13. Sample Test Source (STS). This is the final form of the sample that is used for nuclear counting. This form is usually specific for the nuclear counting technique used in the method, such as a solid deposited on a filter for alpha spectrometry analysis.

4. Interferences

4.1. Radiological: Čerenkov counting measures photons generated by high energy beta particles passing through the final test solution regardless of the radionuclide. The threshold beta particle energy that can produce Čerenkov radiation with a counting efficiency of ~6% is ~ 900 keV.[1] Therefore, radionuclides other than ^{32}P in the final test sample solution having maximum beta emissions greater than 900 keV would likely cause measurable interferences and bias results high. Below 900 keV, the efficiency for Čerenkov counting decreases significantly. Table 17.1 lists some other radionuclides that have sufficient high-energy beta emissions to be counted efficiently by Čerenkov counting. This method provides a technique for the chemical purification of phosphorous from these other potential radionuclides (e.g., fission products, ^{40}K and decay products of the natural occurring series) having sufficient beta energies to produce Čerenkov radiations. Although it is unlikely that these radionuclides would accompany ^{32}P in a RDD, it is important that the method discriminate against them in the final sample test source. Radiological interferences in the final sample test source can be evaluated by counting the test source solution approximately 7 days from the first count, and also by examining the energy distribution in the liquid scintillation spectrum. The second count should produce a net count rate that is ~ 71% of the count rate of the first test source measurement. Inferences also may be detected by examining the energy distribution in the individual sample spectra and comparing it to the expected, interference-free spectrum.

4.2. Non-Radiological: High levels of phosphates (>0.1 mg/L) in the water are accounted for by the relative yielding technique used in this rapid method. If suspended solids are observed or known to exist in the sample, the sample should be filtered through a 0.45-µm filter before proceeding with the method.

5. Safety

5.1. General

[1] See Section 4.5.1 of NCRP Report No. 58, reference 16.7). A state-of-the art liquid scintillation counter may have a better response to the Čerenkov radiation and provide higher detector efficiencies than those stated in the reference.

5.1.1. Refer to your safety manual for concerns of contamination control, personal exposure monitoring, and radiation dose monitoring.
5.1.2. Refer to the laboratory chemical hygiene plan (or equivalent) for general safety rules regarding chemicals in the workplace.

5.2. Radiological

5.2.1. Hot Particles (DRPs)

5.2.1.1. Hot particles will be small, on the order of 1 mm or less. Typically, DRPs are not evenly distributed in the media and their radiation emissions are not uniform in all directions (anisotropic). Filtration using a 0.45-µm (or finer) filter will minimize the presence of these particles.

5.2.1.2. Care should be taken to provide suitable containment for filter media used in the pretreatment of samples that may have DRPs because the particles become highly statically charged as they dry out and will "jump" to other surfaces, causing contamination.

5.2.1.3. Filter media should be individually surveyed for the presence of these particles and this information should be reported with the final sample results.

5.2.2. For samples with detectable activity concentrations of this radionuclide, labware should be used only once due to potential for cross contamination.

5.3. Procedure-Specific Non-Radiological Hazards

- None

6. Equipment and Supplies

6.1. Analytical balance with a 0.001-g readability or better.
6.2. Toploader balance with a 0.1-g readability
6.3. Beakers, Pyrex® – 250, 400 mL
6.4. Hot plate, or other suitable device for reducing sample volume
6.5. Glass stirring rods
6.6. Graduated cylinders – 25, 50, 100, 250, 1,000 mL
6.7. Pipettes, volumetric / automatic: assorted volumes down to the microliter range.
6.8. Scintillation vials – 22 mL glass

NOTE: It has been demonstrated that plastic vials yield a higher efficiency for Čerenkov counting than do glass vials.

6.9. Volumetric flasks – 25, 100, 200, 500, 1,000 mL.
6.10. Detector capable of measuring Čerenkov radiation – Liquid scintillation counter
6.11. Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES)

7. Reagents and Standards

NOTES: All reagents are American Chemical Society (ACS) reagent grade or equivalent unless otherwise specified.
Unless otherwise indicated, all references to laboratory water should be understood to mean ASTM D1193 Type I Reagent water (see Reference 16.3).

7.1. Cation exchange resin: DOWEX 50WX8 50–100 mesh, 10mL
7.2. Diphonix® resin (Eichrom): 100-200 mesh, 2.0 mL
7.3. Hydrogen peroxide (H_2O_2): (30%)
7.4. Demineralized water (DM)

7.5. Carrier solution: Commercially available ICP standard for phosphorus diluted to1.00 mg/mL P, or an approximate 10 mg/mL P solution prepared from $Na_3PO_4 \cdot 12H_2O$ standardized using the ICP-AES and diluted to 1.00 mg/mL P.

7.6. Nitric acid (HNO_3): concentrated (16 M). Note: HNO_3 can degrade forming colored contaminants (nitric oxides) which will interfere with Čerenkov counting. A new bottle of HNO_3 free of color contaminants should be used.

7.6.1. Nitric acid (HNO_3): 2 M; dilute 250 mL of concentrated HNO_3 to 500 mL with DM. Cool and dilute to 1,000 mL with DM.

8. Sample Collection, Preservation, and Storage

8.1. Collect a 1 liter sample in the field in a suitable container.

8.2. No sample preservation is required if sample is delivered to the laboratory within 3 days of sampling date/time.

8.3. If the dissolved concentration of ^{32}P is sought, the insoluble fraction must be removed by filtration before preserving with acid.

8.4. If the sample is to be held for more than 3 days, concentrated HNO_3 shall be added to achieve a pH < 2.

9. Quality Control

9.1. Batch quality control results shall be evaluated and meet applicable analytical protocol specifications (APS) prior to release of unqualified data. In the absence of project-defined APS or a project-specific quality assurance project plan (QAPP), the quality control sample acceptance criteria defined in the laboratory quality manual and procedures shall be used to determine acceptable performance for this method.

9.1.1. A laboratory control sample (LCS) shall be run with each batch of samples. The concentration of the LCS shall be at or near the action level or level of interest for the project.

9.1.2. One method blank shall be run with each batch of samples. The laboratory blank should consist of laboratory water.

9.1.3. One laboratory duplicate shall be run with each batch of samples. The laboratory duplicate is prepared by removing an aliquant from the original sample container.

9.1.4. A matrix spike sample may be included as a batch quality control sample if there is concern that matrix interferences may compromise chemical yield measurements or overall data quality.

9.2. This method is capable of achieving a u_{MR} of 150 pCi/L at or below an action level of 12,000 pCi/L.

9.3. This method is capable of achieving a φ_{MR} 13% above 12,000 pCi/L. This may be adjusted if the event specific MQOs are different.

9.4. This method is capable of achieving a required minimum detectable concentration (MDC) of 3 pCi/L, provided that a minimum sample size of 500 mL is used and a count time of at least 100 min is performed.

10. Calibration and Standardization

10.1. Initially set up the liquid scintillation spectrometer according to the manufacturer's recommendations. The energy range of the spectrometry system should be capable of

measuring in the region of interest (ROI) between 30 and 2,000 keV. Go to Step 10.3 to establish the ^{32}P ROI energy window that will be used to analyze 15-mL samples of a 2-M HNO_3 sample test source.

10.2. Conduct a final set up of the Liquid Scintillation Spectrometer for use to count samples according to ASTM Standard Practice D7282, Section 9.4, "*Liquid Scintillation Counting Initial Instrument Set-up*" (see Reference 16.5). Continuing Instrument Quality Control Testing shall be performed according to ASTM Standard Practice D7282, Section 25, *Quality Control for the Liquid Scintillation Counter*

10.3. Liquid Scintillation Counter Region-of-Interest Setup

10.3.1. The normal photomultiplier high voltage and amplifier gain settings used for liquid scintillation counting (LSC) are satisfactory for Čerenkov counting. In modern LS counters, the beta/Čerenkov radiation interactions in the test sample generate photons detected by photomultiplier tubes (PMT). The PMT in turn converts the detected photon energy voltage pulse which is amplified and transferred to an analysis component of the counter. The voltage pulses are separated by voltage height and digitally converted into an energy spectrum through the use of a multichannel analyzer. The resulting energy spectrum is divided into energy channels; the number of energy channels covers the maximum beta particle or Čerenkov energy of interest (e.g., 4000 channels for 0 to 2,000 keV). For most applications, a ROI of the spectrum is selected for a given radionuclide. Because of the relatively lower number of photons generated and the lower photon-to-electron generation ratio compared to LSC, the maximum beta energy needed for most *practical* Čerenkov counting is about 1,000 keV, although radionuclides having lower maximum beta energies can be measured.[2] The Čerenkov counting efficiency for ^{32}P (β_{max} = 1710 keV) is expected to be ~ 55%.

10.3.2. In a similar manner for LSC instrument set up, the ROI to be used for the qualitative and quantitative determination of a ^{32}P must be established prior to instrument calibration and radionuclide quantification. The figure of merit (FOM; efficiency^2/background) concept shall be used to determine the most advantageous ^{32}P ROI. Once established, the ROI must be maintained during the operation of instrument. A quality control chart using a $^{90}Sr/Y$ source should be used to ensure the ROI counting efficiency of the instrument has not changed and the ^{32}P ROI has not shifted.

10.3.3. The same LSC setting, LS vial type, sample volume, and acidic concentration must be maintained during the establishment of the ROI and instrument calibrations for ^{32}P and instrument background.

10.3.4. The volume to the shoulder of the LSC vial is very reproducible. Using this as a volumetric measure for the standards and samples saves time, sample handling, and reduces potential for cross-contamination. Each laboratory should measure this volume gravimetrically on their own. Typically, this measurement shows a variability of less than 2%.

[2] See Section 4.5.1 of NCRP Report No. 58, Reference 16.7. Radionuclides with lower beta maximum energies can be measured, but efficiencies are quite low.

10.3.5. Set the lower level discriminator of the LSC instrument to eliminate excessive noise signals that give rise to low-energy counts. This setting will vary depending on the instrument manufacturer.

10.4. ^{32}P Region of Interest Determination

10.4.1. Count a ^{32}P background vial containing 15.0 mL of 2 M HNO_3 for 400 minutes. Label the vial and spectrum as $^{32}P_{BKG}$ and electronically save the spectrum.

10.4.2. Use the ^{32}P spectrum generated from the LSC Calibration (Step 10.3.2), set the upper ROI channel to the end point channel of the ^{32}P energy distribution, $^{32}P_{EPC}$. Sum the number of counts from channel 10 to $^{32}P_{EPC}$ and divide by the counting time. Note this as $^{32}P_{gcpm1}$.

10.4.3. Using the $^{32}P_{BKG}$ spectrum from the background sample vial, sum the number of counts from channel 10 to $^{32}P_{EPC}$ and divide by the counting time. Note this as $^{32}P_{BKGcpm1}$

10.4.4. Calculate the relative FOM value as:

$$\left({}^{32}P_{gcpm_1} - {}^{32}P_{BKGcpm_1}\right)^2 \Big/ {}^{32}P_{BKGcpm_1} \quad (1)$$

Record this as the $^{32}P_{FOM_1}$ value.

10.4.5. In a stepwise manner, gradually increase the lower channel included in the ROI and sum the counts in a new ROI (e.g., channel 20 to $^{32}P_{EPC}$) for the ^{32}P and $^{32}P_{BKG}$ spectra. Calculate ^{32}P $gcpm_{2,}$ $^{32}P_{BKGcpm2}$ and $^{32}P_{FOM_2}$. Continue decreasing the ROI by incrementing the lower channel by 10 and calculate ^{32}P $cpm_{i,}$ $^{32}P_{BKGcpmi}$ and $^{32}P_{FOM_i}$ values.

10.4.6. Review the $^{32}P_{FOM_i}$ values and select the ROI with the highest FOM value. Record the ROI as the ^{32}P ROI and use this window when calibrating the unit for ^{32}P detector efficiency as provided in Equation 1.

10.5. ^{32}P Region-of-Interest Counting Efficiency

10.5.1. Using the $^{32}P_{BKG}$ spectrum obtained in Step 10.4.1, calculate the background count rate in the $^{32}P_{ROI}$.

10.5.2. Prepare a calibration source by adding an appropriate amount of traceable ^{32}P concentration (at least 1,000 dpm) in a 5 mL solution of 8 M HNO_3. Bring the final solution volume to 15.0 mL with DM water. Note the reference time and date of preparation and reference concentration (dpm) in the sample.

10.5.3. Count the ^{32}P vial to obtain at least 10,000 counts in the same ROI energy window optimized for ^{32}P as determined in Step 10.4.6.

10.5.4. Calculate the ^{32}P ROI fractional detection efficiency using the following equations:

$$\varepsilon = \frac{\left(R_s - R_b\right) \times DC}{AC \times V \times DF} \quad (2)$$

where

$$DF_s = e^{-\lambda_{P\text{-}32}(t_1 - t_0)} \quad (3)$$

$$DC = \frac{(\lambda_{P-32})t_c}{(1-e^{-\lambda_{P-32}(t_c)})} \quad (4)$$

ε = detection efficiency for ^{32}P
R_s = gross ^{32}P ROI count rate (cpm) for the working calibration source
R_b = count rate (cpm) of the background subtraction sample in the ^{32}P ROI
AC = concentration (dpm/volume or mass) of the ^{32}P standard solution as of its reference date
V = amount (volume or mass) of the standard solution added
DF = correction factor for decay of the standard from its reference date through the measurement of the vial
DC = correction factor for decay during counting
λ_{P-32} = decay constant for ^{32}P, 3.375×10^{-5} min^{-1}
t_0 = reference date and time for the ^{32}P standard
t_1 = date and time of the start of the Čerenkov counting measurement for the ^{32}P standard
t_c = counting time in minutes

11. Procedure

11.1. Water Sample Preparation

11.1.1. As required, filter enough sample volume through a 0.45-µm filter to provide at least 200 mL for radiochemical analysis and sufficient volume for ICP-AES analysis.

NOTES: A volume of at least 500 mL will be necessary to achieve a detection limit of 3 pCi/L. If the 3 pCi/L LLD is to be achieved in subsequent steps:

A sample volume of 500 mL should be used.

All additions of chemical volumes should be scaled up by a factor of 5.

11.1.2. Transfer 150 mL of the filtered sample to an appropriate container.

11.1.3. If not acidified in the field, add sufficient concentrated HNO_3 to the sample to reach a pH of less than 2.0. This usually requires about 0.3 mL of HNO_3 per 150 mL of sample.

11.1.4. Add 1.0 mL of the 1.00 mg/mL phosphorous carrier solution to the beaker and swirl to mix.

11.1.5. Use an aliquant of the sample to determine the phosphorus concentration in µg/mL by ICP-AES. Record the concentration as P_{conc_1}.

11.1.6. Prepare a 10-mL cation exchange column in tandem with a 2 mL Diphonix® column.

11.1.7. Pass about 20 mL of the sample solution through the tandem column arrangement and discard the eluate.

NOTES: This volume is sufficient to equilibrate the columns with the sample solution.

The flow rate through the columns may be controlled using devices such as a vacuum box or peristaltic pump. The flow rate should not exceed about 5 mL/minute.

11.1.8. Pass the remaining sample solution through the columns and collect the eluate in an appropriate container.

11.1.9. Measure a known volume (approximately 100 mL) of the sample which has passed through the columns into a 250 mL beaker for performing evaporation and digestion on a hot plate.

11.1.10. Add 10 mL of 30% H_2O_2 and 10 mL of concentrated nitric acid.

11.1.11. Bring the solution to near boiling and reduce the volume to between 2 and 5 mL.

11.2. Preparation of the sample test source

11.2.1. Transfer the solution to a liquid scintillation vial and rinse the beaker three times with 5-mL aliquants of 2-M nitric acid.

11.2.2. Bring the level in the liquid scintillation vial to the shoulder of the vial (refer to Step 10.3.4), cap, and invert several times to mix.

11.2.3. Count the liquid scintillation vial for a period of time sufficient to achieve a u_{MR} of 150 pCi/L.

11.2.4. After counting the sample test source, remove an aliquant and determine the phosphorous concentration (µg/mL) by ICP-AES. Record the concentration as P_{conc2}.

12. Data Analysis and Calculations

12.1. Equation for determination of final result, combined standard uncertainty, and chemical yield (if requested):

The activity concentration of an analyte and its combined standard uncertainty are calculated using the following equations:

12.1.1. The ^{32}P activity concentration (AC) is calculated as follows:

$$AC = \frac{(R_a - R_b) \times DC}{2.22 \times \varepsilon \times Y \times V \times DF} \quad (5)$$

where:

$$DF = e^{-\lambda_{P\text{-}32}(t_1 - t_0)} \quad (6)$$

$$DC = \frac{(\lambda_{P\text{-}32})t_c}{(1 - e^{-\lambda_{P\text{-}32}(t_c)})} \quad (7)$$

and where:

R_a	=	gross count rate for the sample (cpm) in ^{32}P ROI
R_b	=	background count rate (cpm) ^{32}P ROI
ε	=	efficiency of the detector for ^{32}P ROI
Y	=	fractional chemical yield for phosphorous
V	=	volume of the sample aliquant (L)
DF	=	correction factor for decay of the sample from its reference date until the start of the ^{32}P count
DC	=	correction factor for decay during counting
$\lambda_{P\text{-}32}$	=	decay constant for ^{32}P, 3.375×10^{-5} min^{-1}

t_0 = reference date and time for the sample
t_1 = date and start time of counting the sample
Note: the differential time $t_1 - t_0$ must be in minutes
t_c = counting time in minutes

Note: The elapsed time between the sample count and the reference date must be calculated using the same time units as the decay constant

12.1.2. The standard counting uncertainty of the phosphorous activity concentration, u_{cc}, is calculated as follows:

$$u_{cc} = \frac{\sqrt{\frac{R_a}{t_a} + \frac{R_b}{t_b}}}{2.22 \times \varepsilon \times Y \times V \times DF} \quad (8)$$

where:

t_a = duration of the sample count (min), and
t_b = duration of the background subtraction count (min).

12.1.3. The combined standard uncertainty (CSU) for the ^{32}P activity concentration, $u_c(AC_{P\text{-}32})$, is calculated as follows:

$$u_c(AC_{P\text{-}32}) = \sqrt{u_{cc}^2 + AC^2 \times \left(\frac{u^2(\varepsilon)}{\varepsilon^2} + \frac{u^2(Y)}{Y^2} + \frac{u^2(V)}{V^2} \right)} \quad (9)$$

where:

$u(Y)$ = standard uncertainty of fractional chemical yield for phosphorous,
$u(V)$ = standard uncertainty of the volume of the sample aliquant (L), and
$u(\varepsilon)$ = standard uncertainty of the ^{32}P ROI detector efficiency, ε.

12.1.4. If the critical level concentration (S_c) or the minimum detectable concentration (MDC) are requested (at an error rate of 5%), they can be calculated using the following equations:[3]

$$S_C = \frac{\left[0.4 \times \left(\frac{t_s}{t_b} - 1 \right) + 0.677 \times \left(1 + \frac{t_s}{t_b} \right) + 1.645 \times \sqrt{\left(R_b\, t_b + 0.4 \right) \times \frac{t_s}{t_b} \times \left(1 + \frac{t_s}{t_b} \right)} \right] \times DC}{t_s \times 2.22 \times \varepsilon \times Y \times V \times DF} \quad (10)$$

[3] The formulations for the critical level and minimum detectable concentration are based on the Stapleton Approximation as recommended in MARLAP Sections 20A.2.2, Equation 20.54, and 20A.3.2, Equation 20.74, respectively. The formulations presented assume $\alpha = 0.05$, $\beta = 0.05$ (with $z_{1-\alpha} = z_{1-\beta} = 1.645$), and $d = 0.4$.

$$MDC = \frac{\left[2.71 \times \left(1 + \frac{t_s}{t_b}\right) + 3.29 \times \sqrt{R_b t_s \times \left(1 + \frac{t_s}{t_b}\right)}\right] \times DC}{t_s \times 2.22 \times \varepsilon \times Y \times V \times DF} \quad (11)$$

12.2. Chemical Yield for Phosphorous

12.2.1. Calculate the chemical yield for phosphorous using the information gathered in Steps 11.1.5 and 11.2.4.

The chemical yield of the carrier (Y_P) and its standard uncertainty u(Y_P) can be calculated using the following equations:

$$Y_P = \frac{P_Y}{P_1} \quad (12)$$

where:

P_1 = (P_{conc_1} in µg/mL – refer to Step 11.1.5) × (sample volume used in procedure in mL – refer to Step 11.1.9)

NOTE: P_1 is the mass of P (µg) prior to performing procedure

P_Y = (P_{conc_2} in µg/mL – refer to Step 11.2.4) × (volume of solution in LCS vial in mL – refer to Step 10.3.4)

NOTES: P_1 is the mass of P (µg) added as carrier
P_Y is the mass of P (µg) recovered after completing procedure.

and:

$$u(Y_P) \sim 0.02 \quad (13)$$

Because the yield determination is a relative comparison using the same ICP-AES instrument, the uncertainty budget is related to the precision of the measurements, which is estimated at 2% (assumes that all volumetric dilutions are much less that 2% and thus contribute negligibly).

12.3. Results Reporting

12.3.1. The following items should be reported for each result: sample ID, volume of sample used, carrier yield and its uncertainty, and Čerenkov counting efficiency and its uncertainty.

12.3.2. The following items should be reported for each result:

12.3.2.1. Result in scientific notation ± combined standard uncertainty, critical level, and MDC.

12.3.2.2. If solid material was filtered from the solution and analyzed separately, the results of that analysis should be reported separately as pCi/L of the original volume from which the solids were filtered if no

other guidance is provided on reporting of results for the solids. For example:

^{32}P for Sample 12-1-99:

Filtrate Result: 12.8 ± 1.5 pCi/L

Filtered Residue Result: 2.5 ± 0.3 pCi/L

13. Method Performance
    13.1. Method validation results are to be reported as an attachment.
        13.1.1. Expected turnaround time per batch of 14 samples plus QC, assuming microprecipitations for the whole batch are performed simultaneously:
            13.1.1.1. For an analysis of a 100-mL sample aliquant, sample preparation, ion exchange, digestion and evaporation should take ~ 5.5 h.
            13.1.1.2. Final test source sample preparation for Čerenkov counting takes ~5minutes.
        13.1.2. A 100 minute counting time is sufficient to meet the MQOs listed in 9.2 and 9.4, assuming detector efficiency of ~ 0.35 and chemical yield of at least 0.9. Longer counting time may be necessary to meet these MQOs if the yield is lower.
        13.1.3. Data should be ready for reduction between 8.5 and 10.5 h after beginning of analysis.

14. Pollution Prevention: This method utilizes a Diphonix® resin (~10 mL) and a cation resin (~10 mL). The removal of uranium, thorium, and TRU elements using the extraction column results in the elimination of solvent extraction and other multiple step precipitation and ion exchange techniques.

15. Waste Management
    15.1. Types of waste generated per sample analyzed
        15.1.1. Two mL of Diphonix® resin and 10 mL of cation exchange resins are generated per sample. If a TRU column is used to remove transuranics, this is ~2 mL.
        15.1.2. Approximately 20 mL of acidic waste from the final sample tests source are generated
        15.1.3. Unless processed further, the TRU resin may contain isotopes of uranium, neptunium, and thorium, if any of these were present in the sample originally.
    15.2. Evaluate all waste streams according to disposal requirements by applicable regulations.

16. References

16.1. U.S. Environmental Protection Agency (EPA). 2009. *Method Validation Guide for Qualifying Methods Used by Radiological Laboratories Participating in Incident Response Activities*. Revision 0. Office of Air and Radiation, Washington, DC. EPA 402-R-09-006, June. Available at: www.epa.gov/narel/incident_guides.html and www.epa.gov/erln/radiation.html.

16.2. *Multi-Agency Radiological Laboratory Analytical Protocols Manual* (MARLAP). 2004. EPA 402-B-1304 04-001A, July. Volume I, Chapters 6, 7, 20, Glossary;

Volume II and Volume III, Appendix G. Available at: www.epa.gov/radiation/marlap/links.html.

16.3. ASTM D1193, "Standard Specification for Reagent Water" ASTM Book of Standards 11.01, current version, ASTM International, West Conshohocken, PA. Available at: www.astm.org/Standards/D1193.htm.

16.4. National Council on Radiation Protection and Measurements (NCRP). 1985. Report No. 58, *A Handbook of Radioactivity Measurements Procedures*, Second Edition. Available from www.ncrponline.org/Publications/Publications.html.

16.5. ASTM D7282 "Standard Practice for Set-up, Calibration, and Quality Control of Instruments Used for Radioactivity Measurements," ASTM Book of Standards 11.02, current version, ASTM International, West Conshohocken, PA. Available at: www.astm.org/Standards/D7282.htm.

16.6. Colle, R. 1999. "Chemical Digestion and Radionuclidic Assay of TiNi-Encapsulated ^{32}P Intravascular Brachytherapy Sources," *Applied Radiation and Isotopes, 50*, 811-833.

17. Tables, Diagrams, Flow Charts, and Validation Data

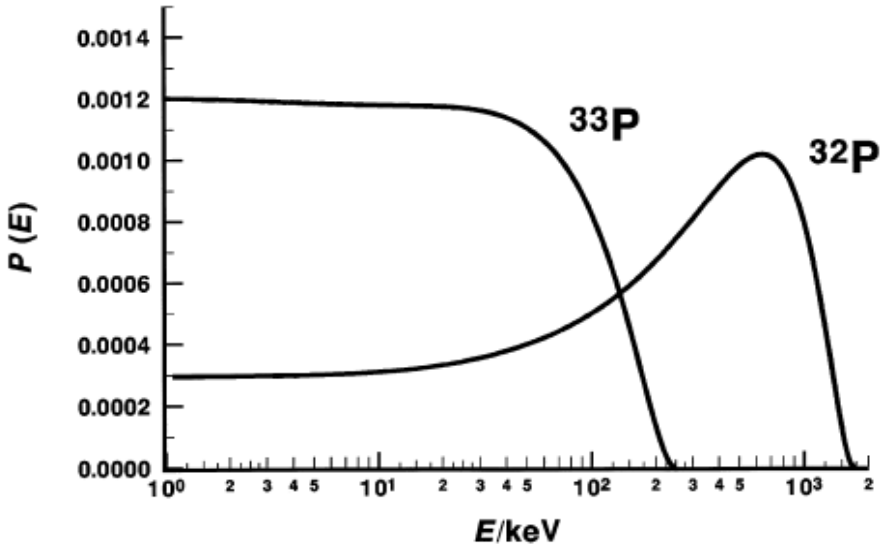
17.1. Table 17.1, Beta Particle Energy and Abundance

Including major radiation emissions from all radionuclides separated.

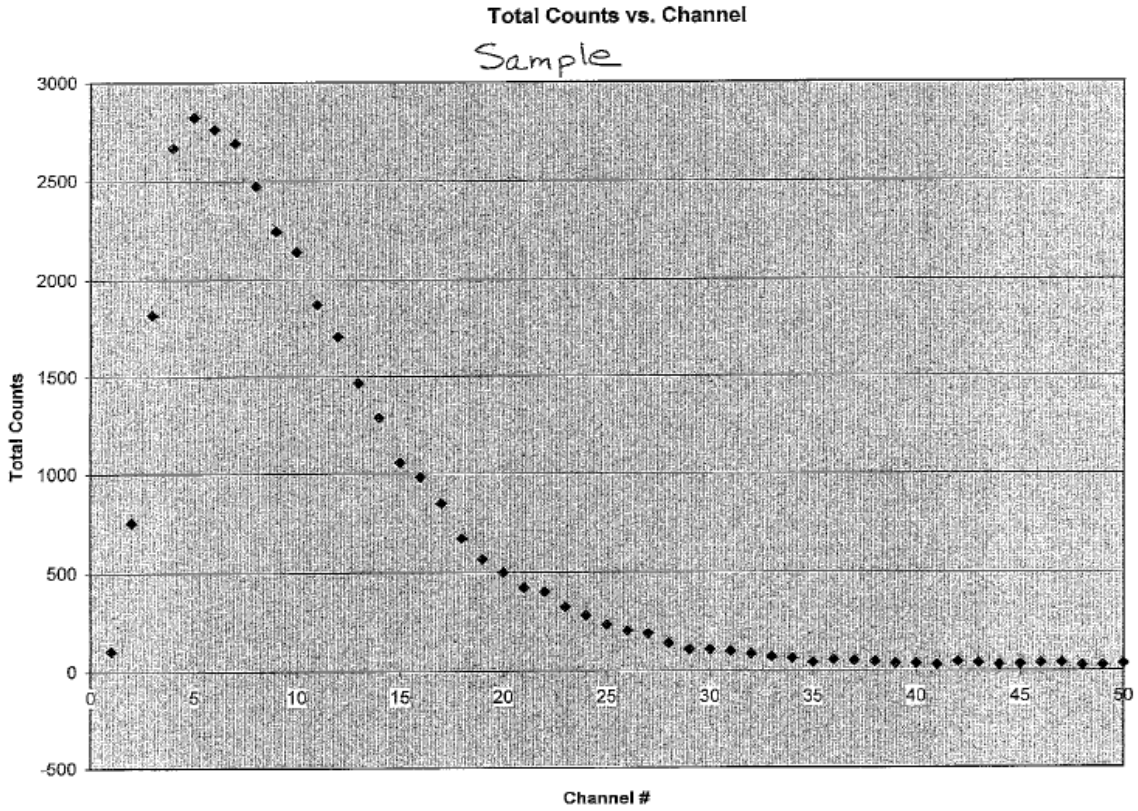
Radionuclide	Half-Life (days)	λ (min^{-1})	Abundance	Energy (keV) Maximum Average
^{32}P	14.262	3.374×10^{-5}	1.00	1710 695
^{33}P	25.34	1.899×10^{-5}	1.00	249 76.4
Potential Radiological Interferences				
^{90}Sr (^{90}Y)	1.05×10^{4}	4.58×10^{-8}	1.00	2280 934
^{89}Sr	50.5	9.53×10^{-6}	1.00	1495 584
^{106}Ru (^{106}Rh)	373	1.29×10^{-6}	0.79	3541 1508
^{140}Ba (^{140}La)	12.75	3.77×10^{-5}	0.20	1679 630
^{40}K	4.55×10^{11}	1.06×10^{-15}	0.89	1311 560
^{137}Cs	1.103×10^{4}	4.38×10^{-8}	0.053	1176 416
^{124}Sb	60.2	8.0×10^{-6}	0.232	2302 918
^{110m}Ag	250	1.93×10^{-6}	0.0129	2892 1199

17.2. Spectra

17.2.1. Spectrum[4] of Mixture of ^{32}P and ^{33}P

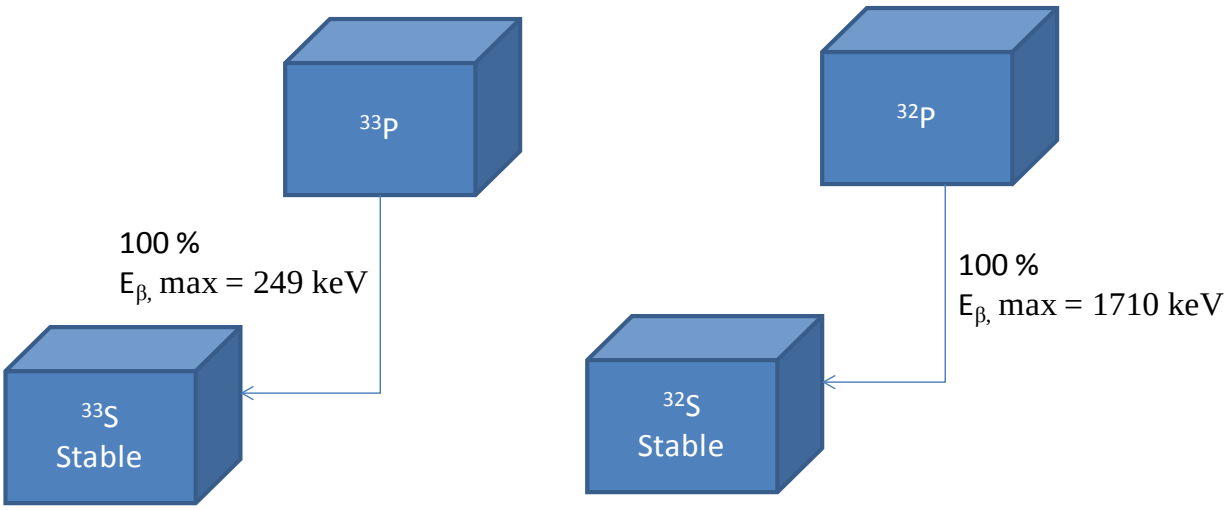


17.2.2. Spectrum of Processed Sample



[4] From "Chemical Digestion and Radionuclidic Assay of TiNi-Encapsulated ^{32}P Intravascular Brachytherapy Sources," Reference 16.10.

17.3. Decay Scheme



17.4. Flow Chart for Separation with Timeline