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LIQUID SCINTILLATION COUNTING TECHNIQUES FOR  
THE DETERMINATION OF SOME ALPHA EMITTING ACTINIDES  
A REVIEW

by

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## ABSTRACT

The present report is a review of the work on liquid scintillation counting techniques, for the determination of alpha emitting actinides like uranium, plutonium, americium etc; for the last three decades (1970-1999). It covers the progress that has taken place in conventional liquid scintillation counting employing various solvents, scintillators and extractants. There is gradual development in instrumentation from integral counting of alpha emitters to alpha liquid scintillation spectrometry to resolve and identify different alpha emitters. These advancements have led to Pulse Shape Analysis (PSA) and Photon Electron Rejecting Alpha Liquid Scintillation Spectrometry (PERALS) techniques for the determination of the alpha emitters in the presence of beta and gamma activity. These techniques allow the determination of actinides at very low levels which has increased their applications to almost all the fields of chemistry; be it biomedical, environmental, geological or process chemistry of nuclear fuels. The development of biphasic technique using various extractants to separate different elements and counting in presence of one another has been made possible. Inorganic scintillators have been recently developed which have the advantage of eliminating effects of quenching and presence of beta / gamma emitting actinides. This review will serve as a reference to those who want to carry out work in the field of determination of actinides using liquid scintillation counting techniques.

# LIQUID SCINTILLATION COUNTING TECHNIQUES FOR THE DETERMINATION OF SOME ALPHA EMITTING ACTINIDES : A REVIEW

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## 1. INTRODUCTION

Liquid scintillation process is based on the conversion of a part of the kinetic energy of alpha / beta / gamma radiation into photons. The photons are counted and related to the concentration of alpha/beta/gamma emitter. The principal use of liquid scintillation counting was the assay of low energy beta emitting nuclides. Alpha emitters could be counted by liquid scintillation counting was also known for long [1].

Alpha emitters, in spite of much lower scintillation yield compared to beta particles, are much more easily counted than beta particles, because alpha particles emit a line spectrum whereas beta spectrum is a continuum. The use of liquid scintillation counting is attractive because of its 100% counting efficiency and simplicity of sample preparation. Alpha particle assay by conventional plate counting methods is difficult because of chemical separation losses and/or self-absorption losses in the final sample may cause either non-reproducible results or create unacceptable errors. Several workers made applications of liquid scintillation counting technique to alpha counting in late 1950s and early 1960s [2-6]; still because of high background, interference from beta particles and very poor energy resolution for alpha energies liquid scintillation counting was not widespread for alpha counting.

Horrocks [6] and Ihle et al [7] obtained a good degree of alpha energy resolution by liquid scintillation technique. This has led to identification and determination of mixture of alpha emitters. However, these methods were not used because detectors and associated electronics were not commercially available and alpha emitting nuclide had to be placed in the scintillator as an organic soluble complex. Therefore, several workers then developed liquid scintillation counting procedure for alpha emitting nuclides based on liquid- liquid extraction and / or the use of a water immiscible scintillator containing an extractant ( extractive scintillator ) [8,9]. The introduction of pulse shape discrimination electronics has allowed the separation of alpha pulses from beta and gamma produced pulses in liquid scintillation systems [10-12].

In these years, gross alpha counting was replaced by differential counting. Instead of single photomultiplier tube, two photomultiplier tubes came in use for coincidence counting to eliminate background noise. Multichannel analysers are being used in liquid scintillation spectrometers to resolve alpha energies. The resolution obtained is about 600-1000 KeV for 4-6 MeV alpha energy range. The development in the counting system is reviewed by Radoszewski [13].

The use of biphasic scintillator solution [115-123] has made determination of one alpha emitter in the presence of other alpha emitter, possible. The use of inorganic liquid scintillators [124-126] can completely eliminate the quenching effect due to acidity and aqueous volume of the sample encountered in the organic scintillators, If the inorganic liquid scintillators are investigated thoroughly, it can be a boon to the field of alpha detection and determination.

This review will comprise of work carried out in the determination of alpha emitting actinides by liquid scintillation counting from the years 1970 to 1999. It will be very interesting to note that there are vast ranges of matrices from which actinides are being determined by using liquid scintillation counting. Various developments have been made in the solvents used, scintillators employed, extractants studied and counting electronics utilised. It will be worthwhile to discuss the basic theory of liquid scintillation counting before describing the methods of determination of alpha emitting actinides using that technique.

## 2. CONVENTIONAL ALPHA LIQUID SCINTILLATION COUNTING TECHNIQUES

### 2.1. BASIC THEORY AND INSTRUMENTATION OF LIQUID SCINTILLATION COUNTING USING ORGANIC SCINTILLATORS

Most of the liquid scintillator solutions are composed of organic solvent and the solute/s. Luminescence ( the emission of light ; visible or UV ) with a characteristic spectrum, following the absorption of radiation (normally of higher energy than the emission), is a property associated with conjugated and aromatic hydrocarbons.

As an ionising particle passes through the solution, excited and ionised solvent molecules are produced. The solvent molecules themselves are very poor scintillators for several reasons, such as 1] Low probabilities for photon emission; 2] The emitted energy range is 2000-3000A<sup>0</sup>, where the used phototubes have reduced sensitivities; 3] High probabilities of re-absorption of emitted photons and 4] The life of excited solvent molecules are relatively long, about 30 ns. Still the solvent molecules act as an efficient means of transferring the excitation energy through the solution to the scintillator/solute molecules.

The role of solute is to trap the excitation energy of the solvent molecules and efficiently release a part of that energy in the form of photon energy. Commonly used scintillators have fluorescence efficiency around 0.90. Since the concentration of scintillator is low, self absorption by solute is also low. Processes that inhibit the energy transfer to the scintillator resulting in loss of light at the detection wavelength, are collectively known as quenching. The probability of quenching is low because of short decay time of excited scintillator molecules (1-2 ns). At relatively low concentration of 3-10 gdm<sup>-3</sup>, the solute molecules are capable of trapping 100% of solvent excitation energy in the conjugated double bond system of aromatic hydrocarbons. Many a times wavelength shifters are added as secondary solutes as they increase the wavelength of emitted photon to 3500-4000A<sup>0</sup> where the common photomultiplier tubes are more sensitive. The mechanism of liquid scintillation and counting statistics is explained in detail in the literature [13,14].

The problem of quenching is continuously being investigated. Very recently, Gomez et al [15] have studied anomalies in quenching evaluation. They have proposed an inner standard procedure which gave adequate results in the application to different kinds of samples.

In a scintillation counter the fluorescence emission produced in a liquid by an ionising particle is detected by a photomultiplier tube. For gross counting of alpha particles, voltage pulses are counted and using a standard source and a calibration curve, alpha emitter can be assayed. This counting technique was further developed for alpha liquid scintillation spectrometry. The voltage pulses obtained from scintillation detectors are directly proportional to the energy absorbed in the scintillator. If all the energy of the alpha particle is absorbed in the scintillator, the energy of the particle can be determined from the size of the voltage pulse. The

single channel spectrometer is a very economic and simple system for alpha energy resolution, although multichannel systems are much faster. There have been specific developments in the instrumentation by Samuel et al [16] and Laney et al [17]. The former have developed an automatic sample changer for alpha liquid scintillation counting and the latter have investigated the two parameter pulse height analysis in liquid scintillation by which chemically quenched samples could be distinguished from colour-quenched samples. Using this principle and instrumentation many actinides have been determined, described as follows.

## 2.2. DETERMINATION OF ALPHA EMITTING ACTINIDES BY CONVENTIONAL LIQUID SCINTILLATION COUNTING TECHNIQUES

Basson et al [1] are the pioneers in the field of alpha standardization with liquid scintillators. They have counted polonium dissolved in 2,5 diphenyloxazole in p-dioxane and uranium dissolved in phenylcyclohexane containing p-terphenyl.

Gibson et al [18] have evaluated liquid scintillation counting as an analytical tool. They have reviewed basic concepts, instrumentation, solvents, scintillators, additives and data handling in liquid scintillation counting. They have hoped that this technique will lead to a wide field of analytical application in chemistry, biochemistry and medicine. They have also noted that the use of this technique is essentially a practical problem, which presents new facts with each new type of sample.

McDowell et al [19] have evaluated the possibility of detecting and identifying alpha emitters in low count-rate samples using some new liquid scintillation counting techniques. They [20] have developed methods of controlling quenching in extractive scintillators for liquid scintillation counting of alpha-emitting nuclides. The quenching effects of 7 extractants were examined and they were found to be in the order tributyl phosphate < di(2-ethyl hexyl)-phosphoric acid  $\approx$  TOPO < didecyl amine sulfate  $\approx$  1-nonyl-decylamine sulfate < trioctyl amine chloride < trioctyl amine nitrate. They [21] have also developed combined solvent extraction-liquid scintillation methods for radioassay of alpha emitters. McDowell [22] has studied high-resolution liquid scintillation method for the analytical determination of alpha-emitters in environmental samples.

McKlveen et al [23] have applied liquid scintillation alpha particle detection to environmental and medical research. The applications include, 1] Monitoring personnel exposed to alpha particle activity; 2] Monitoring biosphere surrounding the possible alpha sources. They have used the technique to determine gross alpha particle activity in the bones of Bat, Cow, Deer, Deerantler, Mouse, Rabbit, Swine and Turkey; in Eggshell, Turtles shell, Hickorynut, Fertilizer; in Human vertebra, coccyx and wisdom tooth. The minimum gross alpha activity was found in the human wisdom tooth ( 0.06 pCi/gm ash  $\pm$  0.01 ).

Horrocks [24] has measured low levels of normal uranium in water and urine by liquid scintillation alpha counting. Amounts of uranium as low as 0.1  $\mu$ g/ml ( $6 \times 10^{-8}$   $\mu$ Ci/ml) were measured. Use of a multichannel analyzer allowed correction for the presence of short-lived beta emitters in the uranium decay chain.

Lefevre et al [25] have investigated alpha detection by liquid scintillation counting. They have developed a fast monitoring system by liquid scintillation counting of liquid wastes, contaminated by plutonium.  $^{241}\text{Pu}$  could be determined in a mixture of  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$ . The different scintillating mixtures and their compatibility with acidic solutions, reductant or oxidant were studied.



Morishima et al [26] have studied determination of uranium in the environmental samples by liquid scintillation counting. The measurement of uranium sample by Cerenkov effect in the medium of distilled water was less sensitive than that by liquid scintillation counting using toluene-dioxane scintillator containing 2,5 Diphenyloxazole (PPO), 1,4-bis-2-(4-methyl-5-phenyloxazolyl) benzene (Dimethyl POPOP) and Naphthalene. Nearly 100% counting efficiency for alpha activity of uranium might be expected in the absence of quenching agents, and minimum detectable limit was 0.43  $\mu\text{g}$  of uranium. The quenching effect due to contamination of  $\text{Fe}^{3+}$  up to about 1.3 mg in samples after anion exchange separation of uranium in environmental samples could be corrected by external standardization method.

Bates et al [27] have reported technique for sequential Cerenkov and liquid scintillation counting after concentration of emitters on submilligram amounts of carrier. The technique was used for the assay of plutonium alpha ( $^{238}\text{Pu} + ^{239}\text{Pu} + ^{240}\text{Pu}$ ).

Mo et al [28] have developed radioanalytical procedures for the determination of Pu, Am and U in the geological samples. The lower limit of detection of  $^{241}\text{Am}$  by this method was 17 pCi and that of total Pu alpha activity was 10 pCi. The average chemical recovery for  $^{241}\text{Am}$  was  $104 \pm 5\%$  and that for the total Pu alpha activity was  $98 \pm 6\%$ . Total U was directly determined in an aliquot of the sample by fluorimetry.

Hands et al [29] have reported simultaneous determination of plutonium alpha and beta activity in liquid effluents and environmental samples. The procedure incorporates an ion-exchange separation followed by extraction with di (2-ethyl hexyl) phosphoric acid and liquid scintillation counting. Magnesium hydroxide is used as a carrier for the concentration and transfer of plutonium between the various stages of the method. Interferences from some other radionuclides have been assessed and the lower limits of detection are about 0.24 pCi and 1.7 pCi for alpha and beta activity, respectively.

Rodwell et al [30] have investigated the distribution of  $^{239}\text{Pu}$  and  $^{241}\text{Am}$  in the Syrian hamster following its intravenous administration as citrate. For plutonium 57% of activity was concentrated in the skeleton and more than 90% in the liver and skeleton after seven days. For americium the liver retained more than 50% of total activity and 25% was excreted in urine within seven days.

Hakanen et al [31] have developed a method for the determination of  $^{241}\text{Pu}$  in the samples of lichen, beard-moss and reindeer liver.  $^{241}\text{Pu}$  results as well as the  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  concentrations were measured. In addition, the activity ratio  $^{241}\text{Pu}/^{239+240}\text{Pu}$  was indicated. During analysis of the fourteen samples analyzed no contamination due to other beta-activities was found.

Miglio [32] has developed a method for the determination of americium, curium and californium in biological samples by combined solvent extraction liquid scintillation counting. He has developed a method to extract Am, Cm and Cf from ashed biological samples dissolved in 8 M  $\text{LiNO}_3$  and  $10^{-2}$  M  $\text{HNO}_3$  into a liquid scintillation cocktail. This new method reduced tissue and instrument background and allowed use of a larger sample for analysis than when a commercial gelling cocktail was used. The extractant cocktail was 20%  $\text{N}_3\text{N}_3\text{N}$ -trioctyl-N-methylammonium chloride dissolved in toluene containing the scintillators p-terphenyl and 1,4-bis-2-(5-phenyl-oxazolyl)-benzene. Several different types of biological samples were analyzed and radionuclide recoveries greater than 90% were obtained in all cases.

Steinkruger et al [33] have performed experiments involving  $^{238}\text{PuO}_2$  and the environment. The interactions of  $^{238}\text{PuO}_2$  with terrestrial and aquatic environments have been examined. The samples from terrestrial experiments were acidified, reduced in volume and

analyzed by liquid scintillation counting while aquatic samples were diluted and counted by liquid scintillation.

Joshima et al [34] have studied distribution of polymeric plutonium injected intravenously with different amounts in mice. Tissue distribution of intravenously injected polymeric plutonium in mice was studied by liquid scintillation counting.

Tjaernhage [35] has developed a liquid scintillation method to measure the total activity of alpha and beta emitting radionuclides in water samples. The report described a method for measuring the total activity of alpha and beta emitting radionuclides with liquid scintillation in case of a fresh fallout. The report consisted of two parts. The first part described the optimization of the method. The second part contained the protocol for the method for preparedness purposes.

Metzger et al [36] have determined specific activity of uranium and thorium in marketable rock phosphate as a function of particle size. They classified marketable rock phosphate fertilizer from Florida into seven particle size fractions ranging from 149  $\mu\text{m}$  to less than 0.5  $\mu\text{m}$  using a Bahco Microparticle Classifier and air elutriation. The resulting size fractions were assayed for uranium and  $^{230}\text{Th}$  by solvent extraction and liquid scintillation alpha-spectroscopy. Results indicated that the specific activity of uranium and  $^{230}\text{Th}$  increased with decreasing particle size. Maximum activities of 110 pCi/g U and 50 pCi/g  $^{230}\text{Th}$  were found in particles less than 1.0  $\mu\text{m}$  in aerodynamic diameter.

Paine et al [37] have determined plutonium in Rocky Flats fresh water systems. This study was initiated to determine the behavior of plutonium in the fresh water aquatic environs at the Rocky Flats Dow Chemical plutonium fabrication plant, Golden, CO. The sample components consisted of sediment, water, seston, zooplankton, fish, vegetation, and small mammals in close proximity to the aquatic systems and were analyzed by a modified solvent extraction liquid scintillation counting procedure.

Coursey et al [38] have reported the liquid scintillation counting techniques for inorganic radiochemicals. The radioactive impurities in  $\text{La}_2\text{O}_3$  were determined in order to remove them. The content of  $^{227}\text{Ac}$  in  $\text{La}_2\text{O}_3$  was measured by gamma-spectroscopic analysis and extraction liquid scintillation counting. The results obtained from these two methods are concordant.

Guilmette et al [39] have reported the radio-assay of americium and curium in biological material by iso-octyl acid phosphate solvent extraction and alpha liquid scintillation counting.

Schaefer [40] has studied the problems of quenching and detection levels of liquid scintillation counting in excretion analysis. Liquid scintillation counting was applied for the determination of beta and alpha emitters in human urine. To reach optimum conditions the properties of different liquid detector combinations and the interferences by quenching effects of the biological samples were analyzed.

Godoy et al [41] have developed a procedure for the determination of  $^{241}\text{Pu}$  by liquid scintillation counting in the environment of the Karlsruhe Nuclear Research Center. The determination of  $^{238}\text{Pu}$ ,  $^{239+240}\text{Pu}$  and  $^{241}\text{Pu}$  was performed in soil and plant samples and in depth profiles in soil in the second main-wind direction. The dose exposure of the environmental population of the Karlsruhe Nuclear Research Center caused by released  $^{241}\text{Pu}$  was negligibly low.

Hermann et al [42] have studied determination of isotope ratios and concentrations of uranium and plutonium in nuclear fuels. They have described methods for separating uranium and plutonium from irradiated nuclear fuels by extraction and ion exchange as well as for determining element concentration and isotope ratio by spectrophotometry, coulometry,

potentiometric titration, mass spectrometry, alpha spectrometry and liquid scintillation counting. Advantages and disadvantages of the individual methods were discussed.

Sezginer [43] has determined uranium from aqueous samples by liquid scintillation counting. Reasonably accurate results have been obtained for samples having uranium concentration of as low as 0.1 gm/L. The author proposed that this method be used for the uranium ore prospecting programme which involves analyses of a large number of leach and solvent extraction solutions. The author has used instagel, a scintillation compound which formed a stable emulsion gel with organic as well as aqueous samples.

Guo-kuisheng et al [44] have reported an extraction liquid scintillation counting technique for the determination of  $^{233}\text{U}$  in HCl solution. Counting efficiency was about 100%. When the sample volume was above 0.5 ml with a counting rate of over  $2 \times 10^3$  cpm (0.1 micro gram  $^{233}\text{U}$ ), the method could provide a precision of about  $\pm 1\%$ .

Chwistek et al [45] have determined uranium accumulated in bacterial cells by liquid scintillation counting. The radiation emitted by natural uranium isotopes (mainly  $^{238}\text{U}$  and  $^{234}\text{U}$ ) was measured by liquid scintillation counting with natural uranium as an internal standard. Determination of the uranium content of bacterial cells was done either by comparing the radioactivity of the sample with that of standard samples or by using a calibration graph. The method was also used for determination of uranium in isolated subcellular fractions. Most of the uranium was associated with components of the cell membrane (lipids and polysaccharides), but part was bound to nucleic acids and microsomes. The relative standard deviation of the radiometric measurements did not exceed 5%. The method enabled trace amounts ( $10^{-7} - 10^{-6}$  mole) to be determined as well as higher concentration of uranium in aqueous media or associated with whole cells and subcellular fractions of bacteria. Scintillator Unisolve 1 or dimilume-30 was used.

Zhao-Kuidong et al [46] have described the use of a novel scintillator 1-phenyl-3-mesityl-2-pyrazolion (PMP) for counting alpha emitters. The properties of the novel scintillator PMP were described and a comparison was made with other ordinary scintillators. Some results on the use of PMP as a primary solute in liquid scintillation counting for alpha emitters were also reported.

Zhuang-Yongneng et al [47] have discussed the determination of  $^{241}\text{Am}$  by extraction liquid scintillation counting method. Several factors which effect the determination of  $^{241}\text{Am}$  by extraction-liquid scintillation counting were discussed. The interference of other alpha particles and low energy beta particles and its elimination were studied. Organic phosphorus extractants such as HDEHP, HEHEHP were used as extractants. Several solvents were tested and the results indicate that it was feasible to use hydrogenated kerosene instead of xylene (or toluene) as solvent in the determination of alpha particles. The method was accurate and less labour consuming.

Moebius et al [48] have studied determination of alpha emitters using extractive liquid scintillation counting. The methods for the determination of alpha emitters were compared. The use of grid ionization chamber and liquid scintillation counting in combination with selective extraction agents offered a new way for simple and rapid nuclide specific determination of alpha emitters.

Murase et al [49] have measured air luminescence spectra for  $^{210}\text{Po}$ ,  $^{238}\text{U}$  and  $^{241}\text{Am}$  with two commercially available liquid scintillation spectrometers. The average counting efficiencies measured with the two counting systems were found to be 33.3% and 33.7%, respectively. The air luminescence effect on liquid scintillation counting of gaseous alpha emitters is mentioned.

Pluta et al [50] have developed a method of determining  $^{238}\text{U}$  and  $^{234}\text{U}$  isotopic concentration in water by liquid scintillation counting. They have used scintillator Permafluor I which contains 5 g of PPO, 0.1 g of dimethyl POPOP in 1 dm<sup>3</sup> of toluene. This method was based on the simultaneous measurement of the alpha activities of  $^{238}\text{U}$  and  $^{234}\text{U}$  and the beta-activity of the decay products of the  $^{238}\text{U}$  isotope. The lowest detection limit of the method was only 0.3 µg/dm<sup>3</sup> of uranium. This method was used to determine U content of coal mine waters which often contain brines.

McGarry [51] has studied the nuclear fallout and heavy metal deposition in ombrogenous peats in Ireland.  $^{241}\text{Pu}$ , together with Pu (alpha), was measured directly by low level liquid scintillation counting.

Chu-Tiehchi [52] has studied the distribution of naturally occurring radionuclides in Peitou hot spring basin. The distribution of naturally occurring radionuclides in hot spring and river water within the Tatun Volcano Group area were studied by means of liquid scintillation counting method and alpha/beta-spectrometry. The concentrations of uranium, thorium and radium in hot spring are 0.18-6.6 ppb, 0.17-17.8 ppb and 6.6-68 mBqL<sup>-1</sup>, respectively. The concentrations of them in river water are 0.064-3.82 ppb, 0.11-10.9 ppb and 3.49 mBqL<sup>-1</sup>, respectively.

Gascon et al [53] have developed accurate and reliable radiochemical methods for the determination of plutonium, americium and curium in typical waste streams from nuclear power plants. Pu, Am and Cm were separated using anion exchange and coprecipitation techniques. The solution of Am and Cm was electrodeposited and measured by alpha spectrometry. In the case of Pu the solution was divided into two aliquots, one for liquid scintillation counting and the other for electrodeposition followed by alpha spectrometry. To determine the chemical recovery of alpha emitters of the Pu fraction and the Am and Cm fraction, the sample was spiked with  $^{236}\text{Pu}$  and  $^{243}\text{Am}$ . The chemical recovery of  $^{241}\text{Pu}$  was calculated using two different methods which gave reliable results. Analysis of every sample was carried out twice to examine the reproducibility of the analytical methods. The radiochemical yields of Pu and Am ranged from 80% to 100% and from 60% to 80% respectively.

He-Weiyu et al [54] have investigated the determination of Th and U by the extraction liquid scintillation alpha spectrum analysis method. They have introduced a method for assaying Th and U by mixing extraction agent and liquid scintillation combined with alpha spectrum analysis. The method had such advantages as simple sample preparation, high detection efficiency for alpha particles (approx. 98%) and low background counting (<10 cpm). The analytical error and the detection limit is < ± 5% and 5 mg/L respectively.

Kosyakov et al [55] have described a method for the determination of Pu, Am, and Cm in soil by trioctyl phosphine oxide extraction. The method was developed for analyzing samples from territories contaminated by radioactivity from the Chernobyl accident. After preliminary treatment, samples were leached by 7 M HNO<sub>3</sub> + 0.3 M KBrO<sub>3</sub> with heating. Extraction by 0.05 M trioctyl phosphine oxide (TOPO) from 7 M HNO<sub>3</sub> isolated Pu. Extraction chromatography on a column with TOPO and PbO<sub>2</sub> separated  $^{144}\text{Ce}$  and partially Zr, U, and Th remaining in the aqueous phase. Then Am and Cm were extracted by 0.2 M TOPO from 1 M lactic acid + 0.07 M DTPA + 1 M Al(NO<sub>3</sub>)<sub>3</sub>. The alpha activities of both extracts were determined by liquid scintillation counting. The chemical yield of Pu was 85 ± 10%; of Am and Cm, 75 ± 10%.

Morris et al [56] have studied the determination of  $^{234}\text{Th}/^{238}\text{U}$  disequilibrium in fresh water systems. The use of  $^{234}\text{Th}/^{238}\text{U}$  disequilibrium measurements is well established in marine systems and is potentially very valuable in determining the settling velocity of particles in fresh

water systems. However, the much lower uranium concentrations in fresh waters prevent established techniques from being used. An alternative approach, based on a combination of Cerenkov and liquid scintillation counting and alpha-spectrometry has improved the sensitivity of the technique so that fresh water samples can be measured.

Fueeg et al [57] have used alpha liquid scintillation spectrometry for the measurement of uranium/thorium disequilibria in soil samples. A new sample preparation method was developed employing extraction chromatographic resin for measuring  $^{238}\text{U}$ ,  $^{234}\text{U}$ ,  $^{232}\text{Th}$ ,  $^{230}\text{Th}$ ,  $^{228}\text{Th}$  and  $^{226}\text{Ra}$  in soil samples, without using any uranium or thorium tracer for determining the chemical yields. This method was tested by analyzing the two different reference materials, IAEA-375, soil from Chernobyl, as well as IAEA SDA-1, a deep-sea sediment with a high calcium content. For all analyzed radionuclides the recoveries were better than 90% with errors (confidence level of 95%) smaller than 5 %. The minimal detectable concentration ranges between 0.2 and 0.8 Bq/kg, based on a one gram aliquot of sample and 80000 seconds counting time.

So far we have reviewed the methods for the determination of U, Pu, Am etc; in various types of matrices from variety of samples and using different separation techniques prior to the determination of actinides by liquid scintillation counting. The technique employed did not differentiate between the scintillations produced from alpha, beta etc. McDowell et al [10] introduced an advanced technique known as Pulse Shape Analysis [PSA] which can differentiate between the photons produced by alpha particle, beta particle, neutrons and Compton recoil electrons. This has the advantage that measurement of alpha particles can be done in presence of other radiations. Further developments in instrumentation for liquid scintillation counting led to a new technique called Photon Electron Rejecting Alpha Liquid Scintillation Spectrometry [PERALS]. The basic principles of pulse shape analysis and PERALS are given below.

### 3. PULSE SHAPE ANALYSIS

#### 3.1. BASIC THEORY OF PULSE SHAPE ANALYSIS

Analysis of decay times of fluorescence in the scintillators was of great theoretical interest [58-60]. These studies led to scintillation Pulse Shape Analysis [PSA] or Pulse Shape Discrimination [PSD] or Pulse Decay Discrimination [PDD] technique in the field of liquid scintillation counting. Pulse shape analysis allows to recognize types of particles or photons and therefore to count a chosen particle e.g alpha particle in the presence of other radiation. The intensity of photons from a scintillation event as a function of time can be divided into at least two components, fast or prompt and slow or delayed. The prompt component has a decay time of a few nanoseconds, equal to the fluorescence lifetime of the fluorescing species. The slow component has a decay time of about 200-300 ns. Kallmann et al [61] have suggested that relatively slow ion recombination processes in the scintillator might be the indirect cause of slow components. An alternate suggestion by Harrison [62] was that some molecules are initially excited to long lived ( $10^{-7}$  S) triplet states and they give rise to slow components. There was an opinion that the intensity of each (prompt and delayed) component is governed by characteristics of ingredients of the scintillator solution. Voltz et al [63] maintained that delayed component is due exclusively to solvent triplets annihilating and eventual production of delayed solute fluorescence. Spurny [64] suggested that delayed fluorescence is caused by mutual annihilation of solute triplets. Ludwig et al [65] have proposed that the delayed component is due to time lag of ion recombination. Berlman et al [66] have studied the effect of liquid scintillation solutions

on pulse shape discrimination. They have concluded that quarternary scintillators (solvent containing 3 solutes) are most effective for pulse shape discrimination.

The relative amounts of light in the prompt and delayed components are dependent on the specific ionization and hence the type of particle causing it. Alpha particles, fission events, neutrons and protons cause higher specific ionization in the scintillator solution than that caused by beta particles, Compton recoil electrons and X rays. This phenomenon provides the basis for PSA as a means of particle identification. Beta particles, Compton recoil electrons and X rays are sources of prompt fluorescence. Neutrons and alpha particles cause the slow delayed component. As beta particles are about 10 times more effective than alpha in producing light, therefore the beta spectra tend to be located in the alpha spectrum range, although alpha particles have higher energy. These interfering beta spectra can be eliminated from the alpha spectra by employing PSA technique.

The pulse shape analysis technique can be used to detect recoil protons, alpha particles, fission fragments or other charged particles with high specific ionization in the presence of electron or vice versa. The advanced PSA technique has given rise to the Photon Electron Rejecting Alpha Liquid Scintillation spectrometry ( PERALS spectrometry ) .

### 3.2. BASIC THEORY OF PHOTON ELECTRON REJECTING ALPHA LIQUID SCINTILLATION SPECTROMETRY (PERALS)

The PERALS system employs a liquid scintillation detector with, 1] PSD circuitry and 2] direct extraction of activity of interest into a scintillator solution. Since the slow component is quenched by oxygen [67], the scintillator solution is purged with inert gas. The PERALS spectrometer includes a sample holder in a counting chamber, photo-multiplier tube, pre-amplifier, linear amplifier and PSD circuitry to analyse the pulse shape voltage and to generate a gating signal for only the alpha interactions. The technique measures the shape of output of linear amplifier by measuring the time from start of the pulse to some time on its fall. The multi channel analyser is operated in the co-incidence mode for alpha spectra.

There has been a continuous effort to improve the PERALS instrumentation system. Thorngate et al [68] have optimized the detector and associated electronics used for high resolution liquid scintillation alpha spectrometry. Klingler et al [69] have developed a portable photon-electron rejection alpha liquid scintillation spectrometer. Kopp et al [70] have devised a new instrument for better PERALS trademark spectrometry. The authors developed the ORDELA model 8100AB PERALS trademark spectrometer for efficient, rapid, and accurate counting and spectrometry of alpha particles from alpha-emitting nuclides in appropriate liquid extraction scintillators. Hashimoto et al [71] have combined Time Interval Analysis (TIA) and Pulse Shape Discrimination (PSD) for the simultaneous determination of environmental alpha radionuclides using liquid scintillation counting.

PERALS has shown itself to be a very practical instrument for alpha spectrometry and an equal alternative to semiconductor detectors for the analysis of many actinide samples. PERALS spectrometry is an attractive alternative since radionuclides may be extracted into a scintillator in which there would be no self-absorption or geometry problems and in which up to 100% chemical recovery and counting efficiency is possible and detection electronics use energy and pulse shape discrimination to provide discrete alpha spectra and virtual absence of beta and gamma backgrounds [84]. The spectra of alpha and beta emitters can be identified and separated by PSA with a high efficiency for alpha emitter and a very good discrimination for beta emitter,

even if radioactivity of beta emitter is 100 times higher than that of alpha emitter [93-95]. PSA allows measurement of trace yields of different decay modes at the same time: beta-active  $^{234}\text{Pa}$  together with alpha-active  $^{231}\text{Pa}$  and gamma emitting  $^{133}\text{Ba}$  with alpha active  $^{214}\text{Po}$ ; and simultaneous measurement ensures the reliability of the yield determination [98]. Traditional Radiochemistry technique requires 17.5 hr/sample while PERALS procedure uses only 2.5 hrs/sample and limited isotopic information can be obtained from LS spectra of PERALS spectrometry [109]. Sample preparation and mounting in PERALS spectrometry is far easier than that encountered in alpha spectrometry using surface barrier detectors [98]. Conventional liquid scintillation counting system gives energy resolution of 600-1000 KeV FWHM; with PERALS spectrometry the resolution is improved to 250-350 KeV FWHM [98].

Higher background of commercial counters and relative poor energy resolution are main limiting factors for extending the use of LSC techniques in the field of low level radioanalysis [98]. The low resolution of energy spectrum [250-350 KeV FWHM at 4-6 MeV alpha energy range], is the biggest disadvantage of PERALS. Selective solvent extraction is an effective way for improving alpha energy resolution and high extractability, small quenching effect, low background activity, and higher counting efficiency are primary considerations in selection of organic extractants [98].

### 3.3. DETERMINATION OF ALPHA EMITTING ACTINIDES BY PSA AND PERALS

The technology of PERALS spectrometry has been reviewed from time to time [72-82]. The PSA technique has found tremendous applications in the field of determination of alpha emitting actinides by liquid scintillation counting as will be seen in the following literature reviewed.

McDowell et al [83] have discussed liquid scintillation alpha spectrometry and its application to bone and tissue samples. The use of equipment and procedures designed for alpha liquid scintillation counting was shown to allow alpha spectrometry with an energy resolution capability of 200 to 300 keV full peak width at half peak height and a background of 0.3 to 1.0 counts/min, or as low as 0.01 counts/min if pulse-shape discrimination methods were used. Methods for preparing animal bone and tissue samples for assay were described.

McKlveen et al [84-86] have discussed alpha particle analysis using PERALS spectrometry. It was an attractive alternative to conventional plate counting methods since radionuclides were extracted into a scintillator in which there would be no self-absorption or geometry problems and in which up to 100% chemical recovery and counting efficiency is possible. Sample preparation included extraction of the alpha emitter of interest by a specific organic phase soluble compound directly into the liquid scintillator. Detection electronics used energy and pulse shape discrimination to provide discrete alpha spectra and virtual absence of beta and gamma backgrounds. Backgrounds of the order of 0.01 cpm were readily achievable. Accuracy and reproducibility were typically in the 100±1% range. Specific procedures have been developed for gross alpha, uranium, plutonium, thorium and polonium assay.

Cooper et al [87] have used liquid scintillation counting for determination of alpha emitting nuclides of the uranium series. The combination of chemical separation and liquid scintillation counting in the determination of alpha emitting nuclides was discussed. The investigation was confined to samples associated with uranium mining and milling. The scintillation mixture which proved most successful comprised of 200 gm/L naphthalene and 4 gm/L 2-(4-biphenyl-6-phenylbenzoxazole) (PBBO) in toluene. Trioctyl phosphine oxide proved

a suitable extractant for thorium, uranium and polonium. Most investigations centred upon assessment using pulse height analysis, although some preliminary studies have been carried out using pulse shape analysis.

Hinton [88] has developed a multipurpose alpha detection procedure for enriched uranium in urine. Uranium was removed from extraneous elements by anion exchange. The uranium was eluted from the column and extracted into a liquid scintillator before being counted in a PERALS spectrometer. The average recovery was 92% at the 0.9 dpm level.

Noguchi et al [89] have performed low level alpha activity measurements with pulse shape discrimination. Measurement system and the characteristic pulse shape discrimination of alpha and beta rays with liquid scintillation counting were investigated for the purpose of low level alpha activity measurements. Various liquid scintillators for pulse shape discrimination were examined by means of pulse rise time analysis. A new scintillator of low cost and of superior characteristics was found. The figure of merit better than 3.5 in rise time spectrum and the energy resolution better than 9% were obtained for carefully prepared samples. The background counting rate for a sample of 10 ml was reduced to 0.013 cpm/MeV in the range of alpha ray energy 5 to 7 MeV.

Satoh et al [90] have done low level alpha activity measurements with pulse shape discrimination. Liquid scintillation counting of alpha particles with pulse shape discrimination was applied to the analysis of  $^{226}\text{Ra}$  and  $^{239+240}\text{Pu}$  in environmental samples and of alpha emitters in/on a filter paper. The instrument used in this study was either a specially designed detector or a commercial liquid scintillation counter with an automatic sample changer, both of which were connected to the pulse shape discrimination circuit. The figure of merit indicating the resolving power for alpha and beta particles in time spectrum was found to be 5.7 for the commercial liquid scintillation counter.

Doane et al [91] have developed a solvent extraction technique for the analysis of  $^{230}\text{Th}$  using the PERALS spectrometry.

Shaw [92] has developed a procedure for the rapid determination of plutonium content on filters and smears using alpha Liquid Scintillation counting. Alpha liquid scintillation in conjunction with microwave digestion was investigated as a technique for rapid Pu analyses. Advantages offered were short turnaround time and field use with acceptable accuracy. A state of the art PERALS Spectrometer utilizing pulse shape discrimination (PSD), and an oil filled photo-multiplier tube counting chamber with 99.7% counting efficiency and 99.95% rejection of beta and gamma pulses, was used. Relatively clean filter samples could be directly counted in an all purpose scintillator, bis 2-ethylhexyl phosphoric acid (HDEHP), 4-biphenyl-6-phenylbenzoxazole (PBBO), toluene and naphthalene. Laboratory preparation of soil samples and smears with high inert solids content was accomplished by dissolution of the sample in nitric and hydrofluoric acids using a microwave digestion system in teflon pressure vessels. The plutonium in the dissolved sample was extracted into tertiary amine nitrate and counted in a HDEHP or 1-nonyldecylamine sulfate (NDAS) containing extractive scintillant. This method was applicable to the determination of total plutonium in air filters, smears and soils.

Dazhu-Yang et al [93-95] have devised a rapid method for alpha counting with extractive scintillator and pulse shape analysis. The interference of beta and gamma radiation with the determination of alpha emitting nuclides by liquid scintillation counting was examined. The extractive scintillator cocktail TOPO-PPO-Naphthalene-Toluene has been developed for transferring actinide elements into organic scintillator and separating the undesirable materials as well as most beta emitters. The Pulse Shape Analysis (PSA) was applied for the discrimination



of beta radiation. The influences of the cocktail composition on PSA had been studied and compared with that of the commercial cocktail. An analytical procedure was suggested for the rapid determination of actinide elements U, Pu, Am and Cm in the nuclear fuel cycle or in the environmental samples. They had used scintillator cocktail, Instant Scintgel [15 ml] + 20% naphthalene. Mixture samples were, 1]  $^{241}\text{Am} + ^{106}\text{Ru/Rh}$ ; 2]  $^{241}\text{Am} + ^{95}\text{Zr/Nb}$  and 3]  $^{210}\text{Po} + ^{144}\text{Ce/Pr}$ . Results indicated that spectra of alpha and beta emitters can be identified and separated by PSA with high efficiency for alpha emitter and very good discrimination for beta emitter, even if radioactivity of beta emitter was 100 times higher than that of alpha emitter. It was applicable in process stream analysis or monitoring of environmental samples.

Cadieux [96] has performed an evaluation of a PERALS spectrometer for the measurement of alpha-emitting radionuclides. Results from the evaluation of the PERALS spectrometer for alpha particle measurements by liquid scintillation counting in samples from the nuclear fuel cycle were presented. Examples of PERALS spectra of process, waste and environmental samples containing Th, U, Pu and Am from the Savannah River Site were shown. The advantages, disadvantages and limitations of the PERALS technique were discussed.

Miller [97] has developed a rapid, economical and sensitive method for the routine determination of excreted uranium in urine. Processing of several hundred samples per week, with a detection limit of 2.5 mBq/L was reported. The sample was mixed with an excess or equal volume of concentrated hydrochloric acid and the uranium was adsorbed onto an ion exchange resin, where it was purified and eluted. The uranium can then either be electrodeposited for alpha spectrometry or extracted with a scintillant for PERALS spectrometry. The whole method, up to the electrodeposition or extraction, took 2 hours and may be automated using a standard Zymark work station. The method has been validated by analyzing urine samples from uranium workers who have been shown to excrete up to 40 mBq/d of total uranium.

Yu-Yufu et al [98] have suggested an improvement for alpha energy resolution in determination of low level plutonium by liquid scintillation counting. In this work, alpha-energy resolution of 270-290 keV for liquid scintillation spectra of  $^{236}\text{Pu}$  and  $^{239}\text{Pu}$  was attained. Higher background of commercial counters and relatively poor energy resolution are the main limiting factors for extending the use of LSC in the field of low level radioanalysis. Among modern liquid scintillation instruments Quantulus/ LBK, 1220 wallac is one of ideal commercial counter. It has very low background and can record pulse height spectra with PSA technique. Energy resolution was 300 keV at 5-6 MeV energy range. Selective solvent extraction was an effective way for improving alpha energy resolution.  $^{239}\text{Pu}$  (5.15 MeV) and  $^{236}\text{Pu}$  (5.76 MeV) were discriminated with 270-290 keV FWHM value with a variance of 10 keV. They have studied six different types of vials, five made of glass material and one of teflon and teflon was found to be the best.

Saarinen et al [99] have developed methods for the determination of uranium series radionuclides  $^{231}\text{Pa}$  and  $^{226}\text{Ra}$  in rock samples using liquid scintillation counting. These isotopes were separated from uranium and thorium by ion exchange chromatography and measured with a low level, low background liquid scintillation counter using pulse shape analysis. The activity of  $^{226}\text{Ra}$  was measured via its alpha active daughter nuclide  $^{214}\text{Po}$ . PSA allows measurement of yield of different decay modes at the same time: beta active  $^{234}\text{Pa}$  together with alpha active  $^{231}\text{Pa}$  and gamma emitting  $^{133}\text{Ba}$  with alpha active  $^{214}\text{Po}$ . Simultaneous measurement ensures the reliability of the yield determination. Determination limits were 5.3 mBq for  $^{231}\text{Pa}$  and 3.7 mBq for  $^{226}\text{Ra}$ . The methods could be applied to obtain information for interpreting uranium series data.

Levina et al [100] have used low background liquid scintillation alpha/beta spectrometer for the determination of plutonium in fuel samples. Ionizing radiation was selected according to the shape of the scintillation pulse. The background loads in the energy window of  $^{239}\text{Pu}$  alpha spectra were  $0.2\text{-}0.3\text{ min}^{-1}$ . Results were provided for measurements of soil contamination by plutonium isotopes and analysis of borehole samples from the area of Unit IV of the Chernobyl Atomic Power Station.

Venso [101] has developed a simple and inexpensive method for the analysis of uranium activity and mass in water by liquid scintillation counting using alpha/beta discrimination. This method appeared to offer a solution to the need for an inexpensive protocol for monitoring uranium activity and mass simultaneously and an alternative to the potential inaccuracy involved when depending on the mass to activity conversion factor. The utility of this method for the proposed compliance monitoring of uranium in public drinking water supplies was field tested with a survey of drinking water from Texas supplies that had previously been known to contain elevated levels of gross alpha activity.

Eikenberg et al [102] have devised a rapid method for the determination of gross alpha activity using LSC with integrated alpha/beta discrimination. For monitoring of potentially incorporated radioactivity by personnel employed at various nuclear facilities in Switzerland, about 600 urine samples were routinely analysed for gross alpha activity at the Paul Scherrer Institute. The method used so far required several radiochemical separation procedures to minimize self absorption of alpha-particles during gas proportional counting. A new and significantly more efficient technique was presented based on liquid scintillation counting using Packard Model 2500 TR/AB equipped with alpha/beta-discrimination. The method was briefly described as follows: (i) Oxidation of organic substances in nitric acid, (ii) co-precipitation of the actinides as phosphate, (iii) wet ashing, (iv) dissolution in 0.1 M HCl, mixing with a scintillation cocktail and counting in alpha/beta mode. By combining the chemical procedures with LSC, effects resulting from quenching were minimized and the detection limit could be reduced to 1 mBq/250 ml urine when measured for about 8 hours. A high accuracy of the data was obtained, due to (i) complete recoveries of all actinides and (ii) reduction of interfering beta-emitters generally present in urine as  $^3\text{H}$ ,  $^{40}\text{K}$  and  $^{137}\text{Cs}$  (alpha/beta ratio in urine usually  $<10^{-4}$ ) by about three orders of magnitude.

Lips et al [103] have performed environmental monitoring at the nuclear power plant Goesgen by a new LSC/PSA technique. The determination of activity in surface waters and aerosol collectors at the nuclear power plant of Goesgen has been changed from conventional gas flow proportional counting of sample planchets to a new alpha/beta liquid scintillation technique. The advantages of the new method were simplified sample preparation, automatic measurement of different types of sample without surveillance and output of results in pre-defined activity units without further data manipulation.

Bower et al [104] have discussed alpha/beta discrimination liquid scintillation counting for uranium and its daughters. Advances in liquid scintillation counting technologies, such as improved scintillation cocktail formulation and alpha/beta radiation discrimination, make LSC suitable for application in uranium process chemistry. Ease of use, low dose, and the huge dynamic range of LSC are distinct advantages for analytical support of actinide processing. All uranium isotopes decay primarily with alpha radiation emission. The immediate short-lived daughters of  $^{238}\text{U}$  are  $^{234}\text{Th}$  and  $^{234}\text{Pa}$ . These nuclides are beta emitters having energy bands that overlap the uranium bands in a liquid scintillation spectrum. The resolution of these overlapping bands by alpha-beta radiation discrimination was useful for uranium quantification and purity

verification.  $^{234}\text{Pa}$  is a high energy beta emitter that can be further identified and quantified from its Cerenkov radiation. Energy spectra were collected on the Packard 2500AB liquid scintillator analyzer for uranyl solutions in di-isopropyl naphthalene and pseudocumene based scintillator cocktails. These cocktails were found to be less hazardous. Calibration curves were prepared for nitric, hydrochloric, and sulfuric acid media. Base titrations demonstrated the effect of acid quenching on those systems. Ion exchange and water soluble polymer extraction studies were readily followed using liquid scintillation methods. Use of hazardous organic solvents can present an additional burden for mixed waste disposal and waste recovery evaluation. Efficiency of counting uranium in 7N  $\text{HNO}_3$  was less than half that of counting uranium in 6N  $\text{HCl}$  or 4N  $\text{H}_2\text{SO}_4$ .

Leyba et al [105] have studied evaluation of a direct extraction/liquid scintillation counting technique for the measurement of uranium in water. An extraction procedure utilizing alpha liquid scintillation was evaluated for the rapid determination of uranium in aqueous environmental samples. The extraction efficiency of the system was measured under varying chemical conditions including pH. The procedure was evaluated against a traditional radiochemical technique using both laboratory prepared control samples and actual ground water. Finally, the possibility of obtaining isotopic information from the liquid scintillation spectra was also investigated using a curve fitting routine. The procedure used was based upon extraction of uranium from sulfate system. URAEX<sup>TM</sup>, a commercially available extractive scintillator containing a tertiary mixed alkyl amine dissolved in toluene was used. Authors recommended the method as a fast, quantitative technique ideal for routine use in the analysis of aqueous samples which include ground water and surface water. Traditional Radiochemistry technique requires 17.5 hr/sample while PERALS procedure needs only 2.5 hrs/sample. PERALS spectrometer was specifically designed for detection of alpha particles in the presence of beta /gamma background. In its current configuration, it has a 99.7% efficiency for alpha particles with a 99.9% beta/gamma rejection rate. Limited isotopic information can be obtained from LS spectra of PERALS spectrometer. Interferences and pH effect of water samples were studied.

Cadieux et al [106] have determined actinides in environmental samples by photon electron rejecting alpha liquid scintillation. Environmental quality assurance standards and actual water samples were treated by one of two methods; either a two step direct extraction, or for more complex samples, pretreatment by an extraction chromatographic separation prior to measurement of the alpha activity by PERALS. Accuracy of the method of  $\pm 5\%$  was confirmed on a number of sample types at activity levels of a few pCi/L or less. Minimum detectable activities were estimated for counting times up to a week in duration and were as low as 0.003-0.005 pCi/L.

Condren et al [107] have proposed a new approach to quench correction when measuring  $^{241}\text{Pu}$  in the presence of Pu alpha by supported-disc liquid scintillation spectrometry. What has not been clear is how best to correct for the quenching associated with the unavoidable variability in source quality of discs prepared by electrodeposition in the course of the routine analysis of environmental samples. The latter results in a reduction in the detection efficiency for  $^{241}\text{Pu}$  and an increase in the misclassification of alpha events. It also gives rise to a shift of the alpha and beta spectra to lower energies. A novel approach was described in which the shift in the alpha peak, as measured by LS spectrometry, relative to that of an unquenched standard, represented the parameter by which both the alpha to beta cross-talk and the beta efficiency are determined using appropriate sets of quenched standards. The method has been tested with

replicate samples of intercomparison materials and confirmed by thermal ionization mass spectrometry.

Usuda et al [108] have investigated characteristics of sensitivity for in-line detection methods of alpha emitters in solution. In order to directly detect low concentration of alpha emitters in solution by in-line detection methods, characteristics of sensitivity for the following three methods (Liquid scintillation counting, Liquid contact counting and ICP-MS) are discussed by measuring natural and 20% enriched uranium solutions. Liquid scintillation counting: Detection efficiency (epsilon) of the method was very high (42%) and background was lowered by alpha/beta/gamma pulse shape discrimination. The detection limit was, therefore, good (0.05 Bq). The method was effective for monitoring of low level radioactive solution and for identification of the alpha emitters. However, the accuracy was not always good and some waste solvents were produced.

Wierczinski et al [109] have developed a liquid scintillation counting system for the internal measurement of alpha particle energies and the detection of spontaneous fission events on-line in flowing organic solutions resulting from continuous rapid chemical separations by liquid-liquid extraction. The scintillator, dimethyl-POPOP and naphthalene dissolved in toluene, contained the extracting agent, di-(2-ethylhexyl) phosphoric acid or dibutylphosphate. An average alpha-energy resolution of 4.8% FWHM was measured in the energy range 4.78 to 7.69 MeV in stationary as well as flowing organic solutions. Additional features of the system are: (1) detection of spontaneous fission events by larger pulses than produced by alpha-particles; (2) suppression of interfering beta- and gamma-radiation by pulse shape discrimination and pile-up rejection; (3) identification of parent-daughter alpha-alpha or alpha-fission-correlations in decay chains and (4) on-line alpha-energy calibration by spiking the organic phase with 3.96-s  $^{219}\text{Rn}$ -1.78-ms  $^{215}\text{Po}$  milked from a  $^{227}\text{Ac}$  source. In order to increase the detection efficiency, a unit with three detector cells in series was built and tested with  $^{219}\text{Rn}$  and  $^{220}\text{Rn}$ . An on-line model experiment for element 104 was carried out using the alpha-emitter 17s  $^{116}\text{Hf}$  produced by nuclear fusion of samarium with neon and chemically separated by liquid-liquid extraction.

Guo-Yifei et al [110] have developed a technique of extraction-liquid scintillation counting of  $^{239+240}\text{Pu}$  in urine.  $\text{HNO}_3$  and  $\text{H}_2\text{O}_2$  were added to 750 ml urine sample taken from 24 h excreted urine, and the sample was evaporated to near dryness for wet ashing of organic materials.  $^{239+240}\text{Pu}$ , U, Am and rare earth elements in the sample were extracted by 30% TRPO-Xylene. Am and rare earth elements extracted into the organic phase were removed by washing with 5.5 and 0.01 mol/l  $\text{HNO}_3$  respectively. Then, ultima Gold F scintillator was added to the organic phase and alpha-activity was counted in a low background TRI-CARB 2550 TR/AB liquid scintillation analyzer using pulse decay discrimination. Finally, alpha activity in urine was calculated according to the counting efficiency of  $^{239+240}\text{Pu}$  under certain window width.  $^{239+240}\text{Pu}$  activity in urine of professional person from hot cell and plutonium plant was obtained by subtraction of uranium alpha activity in same person urine using laser phosphoroscope analysis. The minimum detectable alpha-activity was 0.7 mBq in 750 ml urine sample. Precision of the method was 3% and chemical recovery was  $(99 \pm 3)\%$ .

Cadieux et al [111] have developed separation and analysis of actinides in environmental samples by extraction chromatography coupled with alpha particle liquid scintillation spectrometry. This work combined simplified extraction chromatography using highly selective absorption resins (EiChrom columns) to partition the individual actinides with the measurement of their alpha particle activities by liquid scintillation spectrometry using the PERALS system.

Water and soil samples along with environmental quality assurance standards were routinely processed by this method with an accuracy of  $\pm 5$  to 20% at activity levels of 0.01 to 0.1 Bq.

Aupiais [112] has performed alpha liquid scintillation measurement of plutonium in solution spiked by  $^{236}\text{Pu}$ . The liquid-liquid extraction method used with alpha liquid scintillation with rejection of beta-emission is strongly dependent on the nature of the aqueous solution containing actinides. He has measured plutonium quantitatively by labelling it with  $^{236}\text{Pu}$ . Two procedures of quantitative extraction have been developed as well as the mathematical fit to obtain accurate results. The limits of detection have been determined for several counting times like for instance 0.2 pg/l after one day of acquisition time. He has applied both procedures successfully for the determination of plutonium in doped drinking water and in solid samples after dissolution.

Pujol et al [113] have studied role of quenching on alpha/beta separation in liquid scintillation counting for several high capacity cocktails. The optimization of alpha/beta separation in liquid scintillation using pulse shape analysis is convenient for the simultaneous determination of alpha and beta emitters in natural water and other samples. In this work, alpha/beta separation was studied for different scintillant/vial combinations and it was observed that both the optimum pulse shape discrimination level and the total interference value (that is, the summed relative interference between alpha and beta spectra) were dependent on the sample quenching and independent of the scintillant/vial combination. These results provide a simple method for modifying the counting configuration, such as a change in the cocktail, vial or sample characteristics, without the need to perform exhaustive parameter optimizations. Also, it was observed that, for our counting conditions, the combination of Ultima Gold AB scintillation cocktail with Zinsser low diffusion vials presented the lowest total interference, namely  $0.94 \pm 0.28\%$ , which was insignificant for the counting of environmental samples.

Salonen et al [114] have described advantages of low-background liquid scintillation alpha-spectrometry and pulse shape analysis in measuring  $^{222}\text{Rn}$ , uranium and  $^{226}\text{Ra}$  in ground water samples. Liquid scintillation counting and pulse shape analysis was used in measuring radon and gross alpha and beta activities in ground water. They used conventional LSC counters for the measurement of radon in water, but low-background LSC spectrometers for the gross activity measurements. The lower limit of detection (LLD) for radon in water was 0.6 Bq/L for a 60 min. count with a conventional counter, but 0.1 or 0.2 Bq/L with the two types of low/background LSC spectrometers equipped with a pulse shape analyser. The gross alpha and beta activity measurements were made using a simple sample preparation method, PSA of a low background LSC and spectrum analysis. The LLD recorded for gross alpha and beta with the two spectrometers were 0.02 and 0.03 Bq/L and 0.2 and 0.4 Bq/L, respectively, for a 180 minutes count and a 38 ml sample volume. The method also enabled the calculation of the uranium and  $^{226}\text{Ra}$  contents in water and indicated the presence of some other long-lived radionuclides ( $^{210}\text{Pb}$ ,  $^{228}\text{Ra}$ ,  $^{40}\text{K}$ ). The LLDs attained by this LSC method were two orders of magnitude lower than the maximum permissible concentrations set for uranium and  $^{226}\text{Ra}$ .

Till now, organic scintillator solutions having only one phase (i.e organic) were reviewed. The organic scintillator solution system usually contains an extractant to extract the alpha emitter from its aqueous aliquot. Many extractants can be used to extract the actinide of interest. Because of the aqueous nature of the sample, solvent extraction is the most convenient technique for sample preparation for liquid scintillation counting. It has also led to biphasic liquid scintillation counting where in both the phases can be counted simultaneously or one

actinide can be counted in the presence of the other. The following literature depicts the trend towards biphasic liquid scintillation counting.

#### 4. DETERMINATION OF ALPHA EMITTING ACTINIDES BY BIPHASIC LIQUID SCINTILLATION COUNTING

Ham et al [115] have proposed a method for the determination of americium and curium in biological samples by extraction and liquid scintillation counting. An extraction system based on mono isooctyl phosphate appeared to be the most promising since the reagent, when present only as an impurity in a solution of di-2-ethylhexyl phosphate in isooctane, will extract americium from dilute nitric acid. Due to the commercial unavailability of mono isooctyl phosphate the studies reported involve the appraisal of a homologue mono 3,5,5-trimethylhexyl phosphate (nonyl phosphate). The method described utilizes the direct extraction of americium and curium from an acidic solution of sample ash into a solution of nonyl phosphate and scintillants in toluene. Liquid scintillation counting was done with both phases present in the vial.

Miglio et al [116,117] have developed a technique for the simultaneous determination of americium and plutonium by liquid scintillation counting. A method for the simultaneous determination of  $^{238}\text{Pu}$  and  $^{241}\text{Am}$  by liquid scintillation counting using a multichannel instrument has been developed. A two phase cocktail was employed that separated  $^{238}\text{Pu}$  from  $^{241}\text{Am}$ . Plutonium was oxidized to the +4 state while americium remained in the +3 state. This difference in oxidation states allowed the extraction of plutonium by bis(2-ethylhexyl) hydrogen phosphate (D2EHPA) into the toluene-based phase of the liquid scintillation cocktail. The americium remained in a 0.15 M  $\text{HNO}_3$  -dioxane based cocktail. Differences in scintillation efficiency between phases gave rise to spectral peaks that did not overlap and also permitted the simultaneous determination of the two isotopes whose energies of emitted alpha particles differed by only 14 keV. Recoveries for each isotope averaged better than 95% even when the ratio of one isotope to the other was 10:1.

Manolkar et al [118,119] have used alpha liquid scintillation counting for the determination of plutonium. Liquid scintillation counting is useful and extensively employed for alpha activity measurement. However, quenching was observed and erroneous results are obtained when the size of the solution aliquot and its acidity exceed certain limits. A simple procedure has been developed to overcome the quenching effect of volume and acidity on alpha counting. To the 5 mL scintillator containing the activity, 2.5 mL of very dilute acid was added and the biphasic solution was counted and the quenching was found to be absent.

Subba Rao et al [120] have studied a binary cocktail for the determination of thorium and natural uranium using liquid scintillation counting. They have used a scintillator cocktail (5% of 30% TBP in dodecane and 0.07% of BBOT in xylene) for determination of thorium and natural uranium which avoided the use of secondary solute. The efficiency obtained by this scintillator was better than PPO/POPOP. The efficiency calculated was 82% for natural uranium and 104% for thorium. For the natural uranium the RSD at 2 mg level was 2.16% and at 8 mg was 1.17%. For thorium the RSDs at 2 mg and 8 mg were 2.64% and 1.94% respectively.

Bomben et al [121] have investigated simultaneous biphasic liquid scintillation determination of americium and plutonium in samples such as air filters, sweep-tests, aqueous solutions and urine. They have followed the method suggested by Miglio et al [116,117].

We have developed alpha liquid scintillation counting technique for the simultaneous determination of Pu and  $^{241}\text{Am}$  in a single aliquot [122,123]. A biphasic technique was developed for simultaneous determination of Pu and  $^{241}\text{Am}$  at sub-microgram level in a single aliquot. A linear calibration curve has been developed for applying this approach with wide range of concentration of americium and plutonium. An uncertainty of less than 3% (at  $1\sigma$  level) is achievable.

We have seen that organic scintillators are very useful in liquid scintillation counting for the determination of actinides. However, they are prone to quenching due to the acidity of the actinide solution. Recently some studies have been reported on the use of inorganic liquid scintillators in which quenching effect is not observed. Moreover, inorganic liquid scintillators have low sensitivity for beta and gamma radiations [124-126]. There is vast scope for research in this field that can be acknowledged through the following literature.

## 5. DETERMINATION OF ALPHA EMITTING ACTINIDES BY INORGANIC LIQUID SCINTILLATION COUNTING

Sharipov et al [124,125] have suggested an aqueous solution of terbium as a scintillator for registration of actinoid alpha radiation. They have found concentrated solutions of  $\text{Tb}^{3+}$  in  $\text{D}_2\text{O}/\text{H}_2\text{O}/\text{HCl}/\text{HNO}_3/\text{HClO}_4$  to possess a high light output of scintillations caused by alpha particles of actinoids. Terbium solution in  $\text{D}_2\text{O}$  was found to have maximum scintillation efficiency. Moreover the inorganic scintillator was less sensitive for beta and gamma radiation.

Pavlicek et al [126] have designed an inorganic liquid scintillator which contains 1 to 30% of an inorganic compound as the basic active component; the compound contains a cation with an atomic number  $> 47$  and a halogen anion. The light yield was found to be 70-150% of the light yield of a standard organic scintillator.

## 6. CONCLUSION

As seen from the review the technique of alpha liquid scintillation counting for the determination of actinides is being used in almost every branch of analytical chemistry; be it biochemical, environmental or radiochemical. It depicts the sheer convenience of the method. Investigators are using different scintillators and extractants. There seems to be interest in investigating biphasic liquid scintillation procedures. The development in the electronics has led to increasing use of PERALS spectrometry which allows simultaneous determination of alpha emitting actinides in presence of beta and gamma emitters. The sensitivity of measurements has increased many folds.

Scientists are using extractants and scintillators as per the requirement of their sample matrix. A number of new extractants are making way in the solvent extractant studies. If they are studied in depth and systematically, for in-situ assay by liquid scintillation counting; simultaneous counting of actinides from their mixtures and low level counting of actinides, the technique will become still more simpler. Detailed studies of inorganic liquid scintillators will open new avenues in radioanalytical chemistry.

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Table 1.  
Lower Limits Of Detection Encountered In The Review

S.No.	Sample	Element	L.L.D.	Ref. No.
1	Water & Urine	Uranium	0.1 $\mu$ g/ml	24
2	Environmental	Uranium	0.43 $\mu$ g	26
3	Geological	Plutonium Americium	10 pCi 17 pCi	28
4	Environmental	Plutonium	0.24 pCi	29
5	Bacterial Cells	Uranium	10 <sup>-7</sup> moles	45
6	Coal water	Uranium	0.3 $\mu$ g/dm <sup>3</sup>	50
7	Rock	Protactinium	5.3 mBq	99

8	Urine	Gross alpha	4.0 mBq/L	102
9	Environmental	Actinides	0.003 pCi/L	106
10	Urine	Plutonium	0.93 mBq/L	110
11	Drinking water	Plutonium	0.2 pg/L	112