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Magnetic iron oxide nanoparticles for the collection and direct measurement of adsorbed alpha-emitting radionuclides from environmental waters by liquid scintillation analysis†

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Abstract

Radioactive contamination, be it from accidental or intentional release, can create an urgent need to assess water and food supplies and the environment, and monitor human health. In the event of such an emergency, rapid and efficient methods may be needed to assess contamination levels in scores of samples within a short time frame. Internalized exposure to radionuclides that decay by alpha (α) emission can be especially hazardous, given the strongly ionizing nature of the α particle. Unfortunately, the determination of α -emitting radionuclides using traditional radioanalytical methods is typically labor and resource intensive and time consuming. In an effort to devise methods that are fast, require little labor and laboratory expendables, and minimize the use of toxic or corrosive reagents, researchers at PNNL have evaluated superparamagnetic nanoparticles as extracting agents for α -emitting radionuclides from chemically unmodified and acidified (pH 2) aqueous systems. It is demonstrated that bare magnetite nanoparticles exhibit strong affinity for two representative α -emitting radionuclides (^{241}Am and ^{210}Po) from two representative aqueous matrices (river and ground water). Furthermore, use of the superparamagnetic properties of these nanomaterials to concentrate the analyte-bearing solids from the bulk aqueous solution has been demonstrated. The nanoparticle concentrate can be either directly dispensed into a scintillation cocktail, or first dissolved and then added to a scintillation cocktail as a solution for an α -emission assay by liquid scintillation analysis. Despite the severe quenching caused by the metal oxide suspensions in the cocktail, the authors have demonstrated that modern liquid scintillation analyzers can report accurate α activity count rates; the upper limits of nanoparticle suspension concentrations in a cocktail are reported for cases wherein normal instrument count mode and a quench correction protocol are used. Discussions are provided on the presented sample processing and analysis method, the improvement (lowering) of minimum detectable activity concentrations using the nanoparticle-based assay method, and the quenching effects of nanoparticle suspensions in a scintillation cocktail.

†Electronic supplementary information (ESI) available: A process flow schematic and a table outlining the overall analytical method that is presented. See DOI: [10.1039/c7ay00247e](https://doi.org/10.1039/c7ay00247e)

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1. Introduction

Environmental contamination and human exposure to radioactive materials are significant concerns resulting from existing and emerging applications and accidents in the nuclear field. As the accidents in Chernobyl, Ukraine and more recently Fukushima, Japan demonstrate, environmental contamination of radioactive material from nuclear power operations is a real and significant hazard that can require large numbers of assays in short periods of time.^{1,2} Additionally, nuclear operations over the past several decades throughout the globe have led to a legacy of nuclear contamination that is dangerous to the environment, nuclear workers and the general population.³ Threats of terrorism involving improvised nuclear devices (INDs) and radioactive dispersal devices (RDDs) in populated areas^{4,5} have brought some urgency to developing radio-analytical methods capable of rapidly assessing large numbers of samples (food and drinking water, environmental, and human excreta) for radiological contamination.^{6,7} Fortunately, few examples of intentional and malevolent releases of radio-active materials exist to date. The incident involving the 2006 murder of Russian dissident Alexander Litvinenko in London using ^{210}Po , a pure α -emitter, is illustrative of the destructive nature of internalized α -emitting radionuclides. Further illustrative is the enormous and complex search for contamination of people and property as a result of this targeted attack.^{8–10}

In order to respond to the accidental or intentional events that result in radiological releases, new methods that are capable of rapidly collecting and measuring radioactive analytes, both in the environment as well as in human populations, are needed. Such methods can be used to screen the extent of human exposure and allow cleanup and mitigation efforts to be focused in the right areas or on the right portions of the population. Furthermore, sample screening may serve to triage samples of highest concern, thus dramatically reducing the number of samples requiring full radioanalytical processing. Current methods for the analysis of environmental contamination and human radiological exposure are time, labor, and resource intensive with a resulting low sample throughput. Work is being carried out to develop methods to improve the speed and reduce the complexity of traditional, laboratory-based radioanalytical methods (*e.g.*, for urine,^{11–15} milk,¹⁶ and environmental samples^{17–20}). Nevertheless, these improved throughput methods still need to be performed in a limited number of dedicated radioanalytical facilities, and they consume limited inventories of laboratory expendables (*e.g.*, separation columns or cartridges).^{21–23}

Of the different types of radioactive decay, α particles are the most difficult to measure when the emissions occur within a condensed phase (solid or liquid). This is due to the short travel distances of α emissions through matter (typically measured in tens of microns). Four α -emission measurement techniques are predominantly used in the radioanalytical laboratory: (1) liquid scintillation (LS) analysis, (2) alpha energy analysis (AEA), (3) gas proportional counting (GPC), and (4) ZnS (Ag) scintillators.^{24,25} LS analysis is a highly sensitive technique for measuring α -emitting radionuclides, with virtually 100% counting efficiency.²⁶ However, pulse height spectral resolution is limited,^{27,28} and quenching within the sample can shift α peaks to lower pulse height channels, degrade spectral quality, and diminish the counting efficiency.^{26,29–32} It is challenging to use LS analysis to identify specific α -emission energies, although this has been demonstrated previously using quench

correction techniques coupled with peak deconvolution.^{27,33–36} LS analysis performed directly on sample solutions is therefore primarily useful for gross α determination. For quantitative analysis of specific α -emitting isotopes using LS analysis, thorough radiochemical separations need to be performed first.^{11,15,30}

Iron(II,III) oxide (magnetite, Fe_3O_4) has a chemically active surface that has seen utility in a growing number of sorbent applications for toxic analyte capture. Analyte capture mechanisms on the Fe_3O_4 surface include simple adsorption on the charged polar surface, ion exchange, and redox reactions.^{37–40} There have been a number of studies showing the efficacy of the metal hydroxyl surface as a sorbent for heavy metal^{41,42} and radioactive analyte species.^{40,43,44} Additionally, Feraheme®, a magnetite nanomaterial coated with polyglucose sorbitol carboxymethylether, has been used as a carrier for the diagnostic radionuclides ^{64}Cu , ^{89}Zr , and ^{111}In for *in vivo* imaging applications (*e.g.*, PET/MRI and SPECT/MRI).^{45,46} It is well known that the actinide elements such as Th, U, Pu and Am bind tightly to iron containing minerals in the environment such as goethite ($\alpha\text{-FeO(OH)}$), hematite ($\alpha\text{-Fe}_2\text{O}_3$), maghemite ($\gamma\text{-Fe}_2\text{O}_3$), and magnetite.^{47–54} Iron oxide nanoparticles (NPs) composed of these or similar mineral phases have been shown to have significant chemical affinity toward the relevant species in even the most complex sample matrixes such as sea water and urine.^{40,44}

The use of magnetic nanoparticles (MNPs) to capture a range of radionuclides from naturally occurring water matrices was recently presented by the authors.⁴⁰ The study demonstrated that naturally occurring and man-made α -emitting radionuclides (Po, Ra, U, and Am) could be sorbed onto MNPs in river, ground, and sea water, as well as human urine, across a range of pH. In addition to Fe_3O_4 NPs, the authors evaluated Mn-doped Fe_3O_4 , which exhibited enhanced analyte extraction properties for these radionuclides while maintaining the useful magnetic attributes. Recently, research has been conducted in the functionalization of MNP surfaces to tailor their performance to a range of needs, including those for nuclear waste and waste water treatment, analytical chemistry, catalysis, biochemistry, and medical applications.^{55–58}

The chemically reactive surfaces of these MNPs facilitate capture of analytes of interest, while their superparamagnetic traits facilitate magnetic collection of the analyte-sorbed material. In an earlier study, the authors demonstrated an *in vitro* radiobioassay method wherein Fe_3O_4 and Mn-doped Fe_3O_4 were used to sequester radionuclides from urine. Then, the radio-nuclide-sorbed MNPs were magnetically concentrated from urine and then used to prepare alpha counting sources for AEA.⁵⁹ The concentrated MNPs were dissolved in acid prior to counting source preparation *via* (1) spontaneous deposition onto metal discs (^{210}Po) and (2) NdF_3 co-precipitation and capture on a filter membrane (^{226}Ra and ^{241}Am).

Herein, the authors demonstrate an even simpler method that employs LS analysis, where (1) MNPs are used to sequester radioanalytes from an aqueous sample, (2) the analyte-bearing MNPs are magnetically concentrated onto the vessel wall and the bulk of the solution is decanted, (3) a concentrated radionuclide-bearing MNP suspension is formed, (4) the suspension is added directly to a scintillation cocktail for (5) α -emission counting by a LS analyzer (see ESI† for a simplified process flow schematic and table). It is demonstrated

here that bare magnetite NPs exhibit strong affinity for two representative α -emitting radionuclides (^{241}Am and ^{210}Po) from two representative aqueous matrices (river and ground water). While it has been previously demonstrated that ^{210}Po has virtually quantitative uptake on Fe_3O_4 NPs between pH ~ 1 –8 solutions, ^{241}Am affinity begins to drop below pH ~ 5 .⁴⁰ Therefore, the method demonstration was performed with unaltered river water pH for ^{241}Am , while the ^{210}Po demonstration was performed at both pH 2 and ~ 8 in ground water. The resulting analyte-sorbed MNPs are then used to form a suspension in the liquid scintillation cocktail so as to demonstrate LS analyzer performance and limitations.

Because LS analysis relies on the production, escape, and detection of scintillation-induced photons, LS analyzer instrument performance can be diminished (quenched) by the presence of agents within the sample that disrupt these processes. The suspension of the metal oxide particles causes significant quenching within the cocktail solution. Nevertheless, it is demonstrated that modern LS analyzers can tolerate a great deal of quench and still report accurate α -emission count rates. The authors compare the LS analyzer performance between analyte-sorbed MNP suspensions in the scintillation cocktail and analyte-sorbed MNPs that are dissolved in acid prior to addition to the scintillation cocktail. Additionally, MNP concentration limits above which quantification of α -emission events becomes problematic (for both normal counting mode and counting with an applied quench curve) are presented. The calculations necessary to convert LS analyzer outputs to original sample analyte concentrations, along with determination of minimum detectable activity concentrations obtained by this method, are provided.

The combined approach of using MNPs to capture and concentrate radionuclides from chemically unmodified aqueous samples, plus direct counting of the resulting MNP concentrate *via* LS analysis, represents a fast and green method for qualitative or semi-quantitative analysis of α -emitting radionuclides from solution. In its simplest form, the method requires only chemically benign Fe_3O_4 NPs (or chemically modified MNPs “tuned” to targeted analytes), a strong magnet, a scintillation cocktail, and a LS analyzer. The authors note that the study presented here was performed using one type of MNPs on filtered aqueous samples that had been artificially spiked with radionuclides. As such, further assessment of the method performance on a range of MNP types to capture a range of radioanalytes from a range of sample matrices is still warranted. Furthermore, analysts would require assurance that if multiple α -emitting radionuclides were present in a sample (*e.g.*, for gross α contamination screening), the MNPs would be capable of sorbing each radionuclide to a high degree. Nevertheless, in the event of a major radiological or nuclear release, simple and rapid radioanalytical methods such as this (that require minimal labor, chemical and expendable supply inputs, and laboratory infrastructure) may be necessary to assess the enormous number of environmental and/or *in vitro* radiobioassay samples that may follow.

[†]Electronic supplementary information (ESI) available: A process flow schematic and a table outlining the overall analytical method that is presented. See DOI: [10.1039/c7ay00247e](https://doi.org/10.1039/c7ay00247e)

2. Experimental

2.1 Reagents and materials

All reagents used in this study were of reagent grade. Hydrochloric acid (37%, Fisher Scientific) working stock solutions were prepared as dilutions into deionized water (18.3 MΩ cm) using a Barnstead E-Pure water purification system (Dubuque, IA). The scintillation cocktail was Ultima Gold™ AB (PerkinElmer, Waltham, MA). Americium-241 (^{241}Am , $E_{\alpha} = 5.443 \text{ MeV}$ (13.1%), 5.486 MeV (84.8%)) and polonium-210 (^{210}Po , $E_{\alpha} = 5.304 \text{ MeV}$ (100%))⁶⁰ standards were obtained from Eckert & Ziegler Isotope Products (Valencia, CA). Columbia River water (CRW) was collected north of Richland, WA; uncontaminated ground water was collected from well 699-49-100C on the Hanford Site, WA (HGW). Water was filtered to $0.45 \mu\text{m}$ using a 47 mm diameter type HA membrane filter (Millipore, Billerica, MA) prior to use. Chemical properties such as pH, conductivity, and alkalinity were previously reported for the two water samples.⁴⁰

Iron(II,III) oxide nanoparticles (Fe_3O_4 NPs) were purchased from Sigma-Aldrich (St. Louis, MO). As previously reported,⁴² the MNPs possessed a particle size of $27 \pm 8 \text{ nm}$, surface area of $42 \text{ m}^2 \text{ g}^{-1}$, and specific magnetization of 81 emu g^{-1} . The iron fraction of the MNPs was determined by first dissolving a known mass in hydrochloric acid followed by analysis of iron by inductively coupled plasma-optical emission spectroscopy (ICP-OES) using a PerkinElmer Optima 5300. The resulting iron fraction was determined to be $0.708 \pm 0.006 \text{ g g}^{-1}$ as reported by O'Hara *et al.*,⁴⁰ a value close to the theoretical iron fraction of 0.724.

2.2. Liquid scintillation (LS) analyzer settings

The LS analyzer (Tri-Carb 3100TR, PerkinElmer) was set up with a region of interest between 2 and 2000 channels. The “transformed spectral index of the external standard” (tSIE) was selected to evaluate each sample prior to sample analysis. tSIE mode exposes the sample to an external radioactive source (in this case, ^{133}Ba) prior to each measurement. Based on the resulting pulse height spectrum obtained by the external source, an algorithm generates a tSIE value, which is scaled up to a maximum value of 1000 (equivalent to a completely unquenched ^{14}C standard). When a quench-correction protocol is configured in the LS analyzer, the tSIE value is employed to apply a detection efficiency (E_d) parameter to sample count rates so that samples can be reported in disintegration rates (reduced tSIE values correspond to reduced E_d values as per the quench curve). Expanded explanations of tSIE are made by Kessler and L'Annunziata.^{26,61}

Samples were counted in normal mode, with coincidence times of 18 ns and a 75 ns delay before burst. A minimum of two LS vessels containing 2 mL deionized water and 15 mL scintillation cocktail were counted with each sample set to determine instrument background count rate. Net sample count rates were determined by subtracting the mean background count rate from each sample; when pulse height spectra are presented, the background pulse height spectra is subtracted.

2.3 LS analyzer performance limitations with MNP/scintillation cocktail suspensions

The scintillation cocktail (15 mL) was added to each of seven polyethylene 20 mL LSC vials. A MNP suspension of 5.0 mg mL^{-1} was prepared in water, sonicated briefly, and shaken vigorously. Volumes of the MNP suspension were promptly added to the vials such that total masses of 10, 5.0, 2.5, 1.25, 0.63, 0.31, and 0 mg MNPs were dispensed into the cocktail solution (representing volumes between 2.0 and 0 mL). Water was added to each vessel so that each vessel contained a total of 2.0 mL aqueous solution. Next, a small volume (20 μL) of a concentrated ^{241}Am standard was spiked into each vessel. The samples were vigorously shaken and counted on the LS analyzer. In addition, a reference standard was prepared by spiking the same volume of the ^{241}Am standard into 2.0 mL of 0.1 M HCl in a glass scintillation vial; it was analyzed using several high purity germanium (HPGe) gamma detectors (Ortec, Oak Ridge, TN) that had been energy and efficiency calibrated for this geometry using NIST traceable standards. The mean ^{241}Am activity obtained using this independent analytical method was used to establish the detection efficiency (E_d) of the MNP suspensions in the scintillation cocktail by LS analysis.

Net LS count rates and tSIE values were determined for each MNP suspension in the cocktail. The observed LS analyzer E_d for each solution was calculated as the ratio of the net count rate (counts per second, cps) divided by the reference ^{241}Am activity (Bq) as determined by replicate HPGe measurements. Next, the same sample vials were used to generate a quench curve so that the LS analyzer could also report sample measurements in disintegration rates (Bq). The quench curve-calculated E_d (y) as a function of observed tSIE parameter (x) was approximated by the 3-parameter sigmoidal curve

$y = 97.30 \left[1 + e^{-(x - 58.21)/3.363} \right]^{-1} (R^2 = 0.904)$, as fitted using SigmaPlot (v. 13.0, Systat Software, Inc.).

2.4 Loading ^{241}Am onto Fe_3O_4 nanoparticles from CRW

The batch contact method for sorbing ^{241}Am from spiked aqueous matrices onto MNPs was performed using the method described previously.⁴⁰ However, instead of 5 mL contact volumes, this process used 60 mL. Briefly, a known activity of ^{241}Am spike was added to 60 mL unpreserved and freshly filtered CRW. The spike was allowed to equilibrate for ~1 h while agitating using an orbital shaker. Analysis of a small volume of the equilibrated solution indicated a total ^{241}Am activity of $2310 \pm 114 \text{ Bq}$ ($38.5 \pm 1.9 \text{ Bq mL}^{-1}$). Next, 6.0 mg of MNPs, added as a 1.0 mL addition of a 6.0 mg mL^{-1} MNP suspension, was added to the solution, and the mixture was allowed to equilibrate for ~4 h on the orbital shaker (MNP concentration = 0.10 mg mL^{-1}).

Following the MNP/spike equilibration interval, the vial was removed from the shaker and the MNPs were concentrated onto the vial wall using $\sim 2.8 \times 2.0 \text{ cm}$ arc-shaped NdFeB (N50) magnets possessing surface fields of $\sim 3550 \text{ Gauss}$ (K&J Magnetics, Inc., Pipersville, PA). A concentrated MNP suspension was then prepared: first, 46.9 mL of the MNP-contacted CRW solution was decanted. Next, the magnet was removed and the MNPs were resuspended in the remaining 13.1 mL with brief sonication and vigorous shaking. The resulting suspension contained a MNP concentration (C_{MNP}) of 0.458 mg mL^{-1} .

The activity concentration of ^{241}Am in the MNP concentrate was then determined. Several aliquots of the homogenized MNP suspension were withdrawn and transferred to glass vials. Concentrated HCl was added to dissolve the MNPs, and the solution was evaporated to incipient dryness under a heat lamp; then the residue was brought to a 2.0 mL volume using 0.1 M HCl. These samples were analyzed using calibrated HPGe detectors (Ortec). The pre- and post-contacted MNP activity concentrations enabled the determination of the distribution coefficient (K_d , mL g^{-1}) of the ^{241}Am on the MNPs in the CRW using eqn (1),

$$K_d = \frac{(C_i - C_f)}{C_f} \times \frac{V}{M} \quad (1)$$

where C_i and C_f are the radioanalyte activity concentrations (Bq mL^{-1}) measured in solution before and after the MNP contact interval, respectively. V is the contacted sample volume (mL) and M is the mass (g) of MNPs added.

2.5 Loading ^{210}Po onto Fe_3O_4 nanoparticles from HGW

Polonium-210 was spiked into ~60 mL HGW (natural pH (8.3) and pH 2.0), where it was equilibrated under gentle agitation for ~1 h. The post-equilibrated ^{210}Po activity was determined by pulling a 1.0 mL aliquot from each 60 mL stock and determining activity by LS analysis. The spiked ^{210}Po activity was $475 \pm 5 \text{ Bq}$ ($7.97 \pm 0.09 \text{ Bq mL}^{-1}$) for the pH 8.3 solution and $510 \pm 12 \text{ Bq}$ ($8.55 \pm 0.19 \text{ Bq mL}^{-1}$) for the pH 2.0 adjusted HGW. Next, 6.0 mg of MNPs (added as a 1.0 mL delivery of a 6.0 mg mL^{-1} MNP suspension) was added to the HGW containing vials using the same method as that described in Section 2.4. After the sorption interval was completed, the MNPs were collected on the walls of the vessels using a magnet, and the MNP-free solutions were decanted until the remaining liquid was 5.4 mL and 5.8 mL for the natural pH and the pH 2.0 solutions, respectively. The resulting concentrated MNP suspension concentrations were calculated to be 1.109 and 1.035 mg mL^{-1} , respectively. The activity concentration of ^{210}Po in the concentrated MNP suspensions was determined by pulling an aliquot from the MNP suspensions, dissolving the particles in HCl, reducing the volume with a heat lamp, diluting to 2.0 mL water, adding 15 mL scintillation cocktail, and counting by LS analysis. The calculated K_d values for ^{210}Po on the MNPs from HGW at the two pH levels was then calculated as in Section 2.4.

2.6 LS analysis of ^{241}Am -loaded MNPs

Scintillation cocktail (15 mL) was added to each of ten polyethylene 20 mL LSC vials. To the first five vials were delivered increasing volumes (0.04–2.0 mL) of the concentrated MNP suspension prepared as described in Section 2.4 (Table 1). The total volume of each scintillation vial was brought to 17 mL using water. The vials were vigorously shaken to mix, and were promptly counted on the LS detector (0.5 h count times), along with a reference vial that contained an ^{241}Am spike, 2 mL water, and 15 mL scintillation cocktail.

Additionally, the same five MNP suspension volumes were delivered to 20 mL glass vials and were dissolved using concentrated HCl, then the solution was taken to incipient dryness under a heat lamp. The resulting ferric chloride salts were dissolved and then quantitatively

transferred to the other five plastic LSC vials using a total of 2 mL of 0.1 M HCl. The vials were vigorously shaken and were counted by the LS analyzer (0.5 h count times), along with a similarly prepared ^{241}Am sample *sans* iron.

For all samples, net count rates and tSIE values were recorded from the LS analyzer. Additionally, the pulse height spectrum from each sample assay was exported from the instrument for peak shape evaluation.

2.7 LS analysis of ^{210}Po -loaded MNPs

Scintillation cocktail (15 mL) was added to each of eight polyethylene 20 mL LSC vials. To each of four vials, increasing volumes of the MNP suspension (0.5–2.0 mL) were added from the ^{210}Po extraction performed from pH 8.3 (samples F–I) and pH 2.0 HGW (samples J–M) that were prepared as described in Section 2.5 (details in Table 4). As with the ^{241}Am sorbed MNP/scintillation cocktail set, the total volume of each solution was brought to 17 mL with water. The vials were vigorously shaken and counted repeatedly on the LS detector under a protocol that employed the quench correction curve described in Section 2.3.

3. Theoretical considerations

3.1 Calculating activity concentration in a sample following a MNP-based analyte collection and measurement method

The activity concentration in the sample (A_{sample} , Bq mL⁻¹) is calculated as per eqn (2),

$$A_{\text{sample}} = \frac{A_{\text{meas}}}{E_V} = \frac{R_{\text{meas}}}{E_d \times E_V} \quad (2)$$

where A_{meas} is the measured activity given by the quench-corrected LS analyzer output (Bq) and E_V is the effective volume (mL) of sample solution being measured. A large E_V is made possible by the sorption of a dilute analyte from a solution onto a small mass of MNPs, followed by the subsequent measurement of the resulting analyte-sorbed MNP concentrate in the scintillation cocktail. In the case where a quench correction protocol is not used and measurement results are obtained as a net radiometric count rate (R_{meas} , cps), A_{sample} is obtained as R_{meas} divided by LS analyzer detection efficiency (E_d , cps Bq⁻¹) and E_V . When an aqueous sample is measured directly in a LS cocktail (no MNP-based analyte concentration method employed), the sample volume added to the cocktail, V (mL), is substituted for E_V .

E_V is the product of three components as defined by eqn (3).

$$E_V = (V_{\text{CMNP}} \times C_{\text{MNP}}) \text{CF}_{\text{analyte}} \quad (3)$$

V_{CMNP} is the volume (mL) of the MNP concentrate added to the scintillation cocktail. C_{MNP} is the concentration of the MNP concentrate (mg mL⁻¹), which is given by eqn (4),

$$C_{\text{MNP}} = m_{\text{MNP}} \times V_{\text{conc}}^{-1} \quad (4)$$

where m_{MNP} is the mass of MNPs added to the sample (mg) and V_{conc} is the volume of the MNP concentrate (mL), which is the solution volume remaining after decanting the bulk of the sample solution following the analyte sorption and magnetic collection steps. The analyte concentration factor (CF_{analyte} , mL mg⁻¹) is the degree to which the MNPs capture an analyte from the sample solution. It is the ratio of analyte concentration on the post-contacted MNPs (AC_{MNP} , Bq mg⁻¹) to the analyte concentration in the original sample solution (AC_{sample} , Bq mL⁻¹), as per eqn (5).

$$CF_{\text{analyte}} = AC_{\text{MNP}} \times AC_{\text{sample}}^{-1} = E_s \times V_{\text{sample}} \times m_{\text{MNP}}^{-1} \quad (5)$$

CF_{analyte} can also be calculated by the sorption efficiency of the analyte onto the MNPs from the sample matrix (E_s),[‡] the volume of the original sample (V_{sample} , mL), and the mass of MNPs added to that sample (m_{MNP} , mg).

3.2 Minimum detectable activity

The minimum detectable activity concentration ($MDA_{\text{Bq/mL}}$) of an α -emitting radionuclide measured directly in an aqueous sample is related to the limit of detection (L_d , counts), LS analyzer count time (t , s), E_d , and the sample volume (V , mL) added to the LS cocktail as per eqn (6).

$$MDA_{\text{Bq/mL}} = \frac{L_d}{t \times E_d \times V} \quad (6)$$

L_d is determined at the 95% confidence interval using the Currie equation as given in eqn (7), where C_b is the background count rate of the detector.⁶²

$$L_d = 4.65\sqrt{C_b \times t} + 2.71 \quad (7)$$

When using the MNP-based analyte concentration and measurement method, the $MDA_{\text{Bq/mL}}$ of an α -emitting radio-nuclide in an aqueous sample is calculated similarly, but sample volume is replaced by the effective volume, E_V , of the method (eqn (8)).

$$MDA_{\text{Bq/mL}} = \frac{L_d}{t \times E_d \times E_V} \quad (8)$$

[‡]Fraction of the NP-sorbed analyte divided by the total analyte in the sample.

4. Results

4.1 LS analyzer performance limitations with MNP suspensions

Samples containing the same activity of ^{241}Am but increasing masses of MNPs were counted on the LS analyzer (15 mL scintillation cocktail + 2.0 mL total water), as described in Section 2.3. The scintillation vials containing the MNP suspensions are shown in Fig. 1A. They contain MNP masses between 0 and 10 mg ($588 \mu\text{g mL}^{-1}$). The observed LS analyzer detection efficiency, E_d , was calculated for each MNP suspension and is plotted in Fig. 1B (○), along with the tSIE (transformed spectral index of the external standard) value reported for each sample (●). Solid lines are modeled fits to the data, which are approximated by 4 parameter Hill functions (SigmaPlot).

Samples containing 0.31–1.25 mg MNPs in the suspension ($18\text{--}74 \mu\text{g mL}^{-1}$) indicated no measurable loss of E_d relative to the control sample that contained no MNPs ($E_d = 0.97 \pm 0.05 \text{ cps Bq}^{-1}$). Between the MNP concentration range of $0\text{--}74 \mu\text{g mL}^{-1}$, the tSIE parameter dropped from 521 ± 2 down to 96 ± 3 . Samples containing MNP concentrations $>74 \mu\text{g mL}^{-1}$ demonstrated a steep drop in the observed E_d ; tSIE values concomitantly dropped to 63 ± 3 with a 2.5 mg ($147 \mu\text{g mL}^{-1}$) loading, then plateaued at ~ 55 for suspension masses up to 10 mg ($588 \mu\text{g mL}^{-1}$). Based on these results, it was determined that MNP/scintillation cocktail suspensions demonstrating tSIE values higher than ~ 100 would provide no negative analytical bias when the samples were analyzed without reference to a quench curve.

Next, a quench curve was prepared using the same spiked MNP suspensions. The objective was to evaluate the extent to which an applied quench curve could reliably compensate for signal suppression at the higher end of the MNP concentration range. Replicate sample counts were performed ($n = 7$) using the quench corrected protocol, and reported activities are plotted in Fig. 2. As expected, the MNP suspension concentrations $<74 \mu\text{g mL}^{-1}$ provided a good prediction of ^{241}Am activity. Additionally, the quench correction protocol was able to compensate for count rate suppression in samples containing up to 2.5 mg MNPs ($147 \mu\text{g mL}^{-1}$), effectively doubling the maximum tolerable MNP concentration in the measurement. Above $147 \mu\text{g mL}^{-1}$, when tSIE parameters were <63 (Fig. 1), the quench was too severe to accurately correct count rates to disintegration rates; replicate LS analyzer reported activities were highly scattered.

4.2 Collection, concentration, and measurement of ^{241}Am on MNPs

4.2.1 Sorption of ^{241}Am onto MNPs from river water.—Americium-241 spiked Columbia River water (CRW, 60 mL) was contacted with 6 mg of MNPs, which resulted in sorption of the spike onto the metal oxides. The MNPs were magnetically separated from the liquid, and $\sim 78\%$ of the liquid was removed *via* simple decanting of the aqueous volume. This resulted in a more concentrated analyte-bearing MNP suspension (C_{MNP} , eqn (4)) of 0.458 mg mL^{-1} . Gamma analysis of several aliquots of this new MNP suspension yielded an activity concentration of $335 \pm 24 \text{ Bq mg}^{-1}$. Given the originating MNP mass and ^{241}Am spike activity concentration of $38.5 \pm 1.9 \text{ Bq mL}^{-1}$, it was determined that the radionuclide sorption fraction was $87.0 \pm 7.6\%$. The calculated distribution coefficient (K_d , eqn (1)) value

of ^{241}Am on the MNPs in CRW was $6.7 \times 10^4 \text{ mL g}^{-1}$ ($\log K_d = 4.8$); this result was in good agreement with the $\log K_d$ values of 4.7 and 5.0 reported previously.⁴⁰ Concentration of the ^{241}Am analyte from the bulk water sample to the MNP concentrate resulted in an analyte concentration factor ($\text{CF}_{\text{analyte}}$, eqn (5)) of $8.70 \pm 0.76 \text{ mL mg}^{-1}$.

The ^{241}Am loaded MNP suspension was then used to evaluate the measurement performance of a LS analyzer instrument under two conditions: (1) when MNPs were suspended in the scintillation cocktail and (2) when MNPs were first dissolved in HCl and the resulting ferric chloride solution (in 0.1 M HCl) was added to the scintillation cocktail. Because the maximum MNP mass added to the scintillation cocktail in this experimental set was $<1.25 \text{ mg}$ ($<74 \text{ } \mu\text{g mL}^{-1}$), and therefore below the range where loss of instrument E_d was observed to occur, this sample set was analyzed without the application of a quench correction protocol.

4.2.2 LS analysis of ^{241}Am loaded MNPs.—The spectral and count rate effects from increasing concentrations of ^{241}Am loaded MNP suspensions in the scintillation cocktail were examined. Table 1 lists the MNP concentration range that was evaluated (samples A to E, 1.1 to $54 \text{ } \mu\text{g mL}^{-1}$). Fig. 3 shows an overlay of each of the five α radiation induced pulse height spectra for those MNP suspensions loaded with ^{241}Am . For comparison, a minimally quenched, MNP-free ^{241}Am standard in the scintillation cocktail was evaluated. The resulting MNP-free pulse height spectrum had a peak maximum (C_{max}) at 643 channels (see “Unquenched” pulse height spectrum in Fig. 3); the tSIE quench parameter was reported to be 520 ± 10 .

Fig. 3 illustrates how the pulse height spectra become increasingly quenched with increased MNP loadings. Table 2 (under “MNP suspensions”) lists the C_{max} channel under each condition, as well as the tSIE value that was obtained immediately preceding the sample analysis *via* the instrument’s internal ^{133}Ba gamma source. The presence of MNPs in the scintillation cocktail caused a substantial drop in tSIE, down to a value of 147 for the $54 \text{ } \mu\text{g mL}^{-1}$ suspension (sample E). The logarithmic function $y = -93.9 \ln(x) + 790$ ($R^2 = 0.989$) approximates the data, where y is tSIE and x is the mass of MNPs (μg) suspended in a 17 mL cocktail + water mixture.

Since the tSIE values for all the MNP suspensions in this experimental set were above the threshold where adverse E_d effects were observed to occur (~ 63 , Fig. 1), there was no concern that negative count rate biases due to quenching would be obtained. Indeed, the observed net count rates, normalized to the mass of MNPs present in the vials, resulted in a mean of $321 \pm 9 \text{ cps mg}^{-1}$ across the entire MNP suspension concentration range (Table 2). Given the independently measured ^{241}Am activity concentration in the MNP suspension ($335 \pm 24 \text{ Bq mg}^{-1}$), the mean LS analyzer E_d was determined to be $0.96 \pm 0.07 \text{ cps Bq}^{-1}$ across the MNP suspension range. This is in good agreement with the E_d reported in Section 4.1 for ^{241}Am -doped MNP suspensions containing 1.25 mg of the metal oxide ($0.97 \pm 0.05 \text{ cps Bq}^{-1}$).

From the information in Tables 1 and 2, the analyte activity concentration of the original sample (A_{sample}) can be calculated as per eqn (2). It is obtained by taking the measured

count rate of the sample (R_{meas} , Table 2) divided by the product of the effective volume (E_V) made possible by the MNP analyte concentration and measurement method (Table 1, eqn (3)) and the E_d obtained in Section 4.1 for MNP concentrations 74 mg mL^{-1} ($0.97 \pm 0.05 \text{ cps Bq}^{-1}$). Table 3 reports calculated A_{sample} along with the analytical bias as compared to the independently determined (*via* HPGe analysis) ^{241}Am activity concentration in the river water.

4.2.3 LS analysis of dissolved ^{241}Am loaded MNPs.—An additional sample set was prepared using the same batch of ^{241}Am loaded MNPs that was employed above. However, the MNPs were first dissolved in HCl, the solution evaporated, and the salts brought up in 2 mL 0.1 M HCl prior to adding to the scintillation cocktail. A faint yellow color, attributed to ferric chloride, was observed only for the sample bearing the highest iron concentration (sample E, Table 2). LS analysis of this set indicated that the C_{max} channel remained rather stable across the ferric iron concentration range, and the tSIE values were consistently 426 (see “Dissolved MNPs” in Table 2). Linear regression was used to approximate the observed tSIE (y) as a function of dissolved MNP mass (x) present: $y = -0.0653x + 478$ ($R^2 = 0.784$). When considering only the actual iron mass remaining from the dissolved MNP residues ($0.708 \pm 0.006 \text{ g Fe per g MNP}$), the regression yields: $y = -0.0922x + 478$ ($R^2 = 0.784$). The approximately linear and modestly decreasing tSIE as a function of MNP mass for acid-dissolved MNPs is in stark contrast to the steeply decreasing tSIE *vs.* the MNP mass curve observed for MNP suspensions in the scintillation cocktail (Section 4.2.2).

When the observed count rates were corrected for the equivalent mass of MNPs present, the average signal was $322 \pm 3 \text{ cps mg}^{-1}$; the slight ferric chloride induced coloration of the scintillation cocktail had no effect on the LS analyzer E_d , as expected. The observed E_d was determined to be $0.96 \pm 0.07 \text{ cps Bq}^{-1}$. These results are in excellent agreement with the E_d observed for the MNP suspensions. Table 3 likewise reports calculated A_{sample} along with the analytical bias as compared to the independently determined ^{241}Am activity concentration in the river water.

4.3 Collection, concentration, and measurement of ^{210}Po sorbed MNPs

4.3.1 Sorption of ^{210}Po onto MNPs from ground water.—In a similar fashion to that described in Section 4.2.1, ^{210}Po spiked Hanford ground water (HGW), at natural pH and pH 2.0§ (~60 mL each), was contacted with 6.0 mg of MNPs ($\sim 0.1 \text{ mg mL}^{-1}$ suspension). ¶ After agitating the mixture for several hours, the MNPs were magnetically separated from the bulk matrix, and ~90% of the post-contacted HGW was discarded. The calculated MNP concentrate suspensions (C_{MNP} , eqn (4)) were 1.109 and 1.035 mg mL^{-1} for the pH 8.3 and pH 2.0 solutions, respectively; these ^{210}Po -loaded MNP mass concentrations were ~2.4 times greater than that prepared for the ^{241}Am -loaded MNP concentrate described above.

§pH ~ 2 simulates field preserved water samples.

¶ Fe_3O_4 NPs were demonstrated to be chemically stable at pH 2 by O'Hara *et al.*, *RSC Adv.*, 2016, 6, 105239–105251.

The ^{210}Po activity concentrations in the concentrated MNP suspensions were independently determined to be $80.2 \pm 1.1 \text{ Bq mg}^{-1}$ (pH 8.3) and $90.7 \pm 2.3 \text{ Bq mg}^{-1}$ (pH 2.0). (see Section 2.5). Residual activity concentrations of $0.3 \pm 0.1 \text{ Bq mL}^{-1}$ were measured for both post-MNP contacted solutions. Based on the initial ^{210}Po activity concentration present in the solutions ($8.0 \pm 0.1 \text{ Bq mL}^{-1}$ and $8.6 \pm 0.2 \text{ Bq mL}^{-1}$), the sorbed fractions were calculated to be $96 \pm 2\%$ and $97 \pm 3\%$, respectively. The K_d for ^{210}Po on the MNPs in the natural pH HGW sample was determined to be $2.4 \times 10^5 \text{ mL g}^{-1}$ ($\log K_d = 5.4$), and the K_d was $2.7 \times 10^5 \text{ mL g}^{-1}$ ($\log K_d = 5.4$) for the pH 2.0 HGW sample. These results are in good agreement with values previously reported by the authors ($\log K_d = 5.4$ to 6.1).⁴⁰ In this example of the use of MNPs to concentrate an analyte of interest from a bulk aqueous sample, the analyte concentration factors ($\text{CF}_{\text{analyte}}$) were $10.0 \pm 0.2 \text{ mL mg}^{-1}$ (pH 8.3) and $10.5 \pm 0.4 \text{ mL mg}^{-1}$ (pH 2.0).

4.3.2. LS analysis of ^{210}Po loaded MNPs.—The ^{210}Po loaded MNP concentrates from the pH 8.3 (samples F–I) and pH 2.0 (samples J–M) solutions described above were used to prepare a range of MNP suspensions in the scintillation cocktail (Table 4). For this experimental set, the MNP concentration range exceeded the level at which E_d was observed to be adversely affected by quenching (up to 2.22 mg ($131 \mu\text{g mL}^{-1}$)). Since it was demonstrated that a quench curve could accurately compensate for the quenching induced by samples containing up to 2.5 mg ($147 \mu\text{g mL}^{-1}$) MNPs (Fig. 2), this set of ^{210}Po loaded MNPs were analyzed using the quench curve described in Section 4.1. Being that the α -emission energies of ^{241}Am and ^{210}Po are very similar (within $\sim 0.18 \text{ MeV}$ of each other), it was expected that the previously generated quench curve would be viable for ^{210}Po -bearing MNP suspensions.

Fig. 4 shows the pulse height spectra of the ^{210}Po loaded MNP concentrates originating from the spiked natural pH HGW solution (samples F–I), plus a direct aliquot (2.0 mL) of the ^{210}Po spiked HGW that was sampled prior to MNP addition. Table 4 provides the MNP masses in the scintillation cocktail and calculated ^{210}Po present in each sample. Table 5 provides the observed pulse height C_{max} channel, tSIE parameter, measured activity (A_{meas}), and sample activity (A_{sample}), calculated as per eqn (2).

When the activities were corrected for the MNP mass present in each suspension, the mean activity concentration of the MNPs used to collect ^{210}Po from the natural pH HGW was $79 \pm 2 \text{ Bq mg}^{-1}$, with a range of $\sim 4\%$ across the sample set. This measured activity concentration is in excellent agreement with the independently determined activity concentration of $80.2 \pm 1.1 \text{ Bq mg}^{-1}$. Similarly, the mass corrected ^{210}Po activity concentration for the sample originating in pH 2.0 HGW was $87 \pm 2 \text{ Bq mg}^{-1}$, with a $\sim 4\%$ range in the data across the sample set. Again, this is in very good agreement with the separately determined activity concentration ($90.7 \pm 2.3 \text{ Bq mg}^{-1}$).

When considering the measured activity of each MNP suspension (A_{meas} , Table 5) and the effective volume (E_v , Table 4) for each sample, the calculated activity in the original sample (A_{sample}) was between 7.7 and 8.2 Bq mL^{-1} for samples F–I and between 8.1 and 8.5 Bq mL^{-1} for samples J–M (Table 5). These are in good agreement with the independently determined sample activity concentrations of $8.0 \pm 0.1 \text{ Bq mL}^{-1}$ (samples F–I) and 8.6 ± 0.2

Bq mL⁻¹ (samples J–M). Analytical biases for samples F–I range between –3.2 and +2.2% and analytical biases for samples J–M range between –4.8 and –0.5%.

5. Discussion

Liquid scintillation analysis is an excellent tool for assessing gross α and β activity in an unprocessed aqueous sample. However, the method is limited by how much sample volume can be solubilized into the scintillation cocktail, and the entire volume of the solution/cocktail mixture is limited to 20 mL for commercial instruments. The minimum detectable activity concentration of a sample is therefore limited by the sample volume analyzed (typically a few mL) and the duration of the measurement. Typical radiochemical processes to concentrate dilute analytes of interest from a bulk aqueous sample include co-precipitation, column separation, liquid–liquid extraction, or simple evaporation; however, each of these processes requires laboratory infrastructure. Demonstrated herein is a simple qualitative or semi-quantitative method to sorb and concentrate α -emitting radionuclides from a sample onto a highly dispersible metal oxide nanomaterial, after which a direct assay of the magnetically concentrated analyte by a LS analyzer is performed. In general, the method may be of value immediately following radiological or nuclear emergencies, when laboratory capacities might be quickly exceeded. At the least, it has the potential to screen or triage samples to reduce the burden on limited laboratory capacity and limited expendable laboratory resources.

5.1 MNPs for analyte concentration and analysis

The described method is capable of concentrating a range of naturally occurring or man-made radionuclides from environmental waters and urine onto a small mass of relatively non-toxic Fe₃O₄ NPs,^{63,64} which in turn can be isolated from the bulk solution by application of a strong magnet.^{40,59} This resulting concentrated metal oxide suspension can then be introduced directly into the scintillation cocktail, or the MNPs can be dissolved prior to scintillation cocktail addition (see ESI† for process flow schematic and table).

In this initial effort, the authors demonstrate the concentration of two representative α -emitting radionuclides (²⁴¹Am and ²¹⁰Po) from 60 mL of artificially spiked river and ground water (at the natural pH and at pH 2) onto a small mass of MNPs (6 mg). Magnetic collection of the MNPs from the sample allowed the majority of the sample volume to be decanted, thus creating an analyte concentration factor (CF_{analyte}) of ~8.7 mL mg⁻¹ for the ²⁴¹Am/CRW example and ~10 mL mg⁻¹ for the ²¹⁰Po/HGW examples.

Analyte concentration factors of ~10 mL mg⁻¹ are useful, but only moderately impressive. However, with further material and method development, greater concentration factors can likely be obtained by a variety of means. These include the use of larger sample volumes, use of less MNP mass, and reduction in the volume of the concentrated suspension. The use of MNPs that have been surface functionalized with extracting ligands is another method to potentially facilitate an increase in the volume of the sample and to increase the analyte specificity of sorption.^{58,65–67}

The method of analyte concentration on MNPs $\rightarrow$ magnetic collection $\rightarrow$ direct assay of analyte-sorbed MNP concentrates by LS analysis (or alternatively *via* an assay of dissolved MNP concentrates) provides an enhanced analyzer signal, which has been defined as the effective volume (E_V). In the simplest LS analysis process, a sample volume is added directly to the scintillation cocktail. The analytical signal is limited by the few milliliters of sample that can be solubilized within that cocktail volume. When analyte-concentrated MNPs are added directly to the scintillation cocktail, the effective sample volume being assayed is significantly enhanced. E_V is increased by adding an increased quantity of analyte-sorbed MNPs to the scintillation cocktail and by using MNPs capable of providing the highest possible analyte concentration factor (CF_{analyte}). However, the mass of MNPs added to the scintillation cocktail must not exceed levels at which E_d is diminished (when not utilizing a quench-corrected protocol) and must not exceed levels at which a quench-corrected protocol cannot reliably compensate the LS analyzer response. The discussion on quenching will be continued in Section 5.3.

The authors point out that it is conceivable that low energy photon spectroscopy (LEPS) may be a viable alternative measurement approach for some actinide-sorbed MNP concentrates. Americium-241, for example, has several low-energy photon emissions, with the most analytically useful emission at 59.54 keV (35.9% intensity).⁶⁰ With an approximate E_d of 10% for a LEPS instrument at this energy, the effective ^{241}Am measurement efficiency would be $\sim 0.036 \text{ cps Bq}^{-1}$. While the sensitivity of LEPS to ^{241}Am is dramatically lower than that provided by LS analysis, LEPS does provide precise photon energy resolution, which in turn results in positive isotope identification. Therefore, a thin planar deposit of the MNP concentrate may provide a viable counting geometry for LEPS-based analysis. However, attenuation of the photons from the Fe_3O_4 NPs ($\rho \approx 5.2 \text{ g cm}^{-3}$) may require a specific instrument calibration.

5.2 MDA comparison between the direct aqueous sample assay and MNP-based analyte assay

Minimum detectable activity concentration ($\text{MDA}_{\text{Bq/mL}}$) of aqueous samples measured directly in the scintillation cocktail is defined by eqn (6). For a given sample volume added directly to the cocktail, the MDA is improved (lowered) by increasing the data acquisition time, t . Due to the asymptotic nature of MDA as a function of count time (MDA decreases as a power function with the data integration time), directly assayed samples may require long count times in order to discriminate a low-level analyte signal from the background count rate (C_b) of the instrument.

Alternatively, when an effective volume (E_V) is obtained by the assay of analyte-sorbed MNPs, the MDA can be dramatically reduced for a given data acquisition time (eqn (8)). Additionally, it was observed that the LS analyzer background count rate (C_b) diminished as a sigmoidal function as the MNP suspension concentration in the scintillation cocktail was increased. Thus, C_b decreases (leading to a decrease in L_d , eqn (7)) as E_V increases. These two factors work in a complimentary fashion to reduce MDA for a given data acquisition time. Fig. 5A shows the observed reduction in C_b as a function of MNP mass concentration in the cocktail. Fig. 5B plots the calculated $\text{MDA}_{\text{Bq/mL}}$ for the MNP concentrations in the

scintillation cocktail for samples F–I (Table 4) for count times between 1 and 120 min. For comparison, the dashed line plots the calculated $MDA_{Bq/mL}$ curve for 2.0 mL of aqueous sample added directly to the scintillation cocktail. The curves consider the reduction in L_d based C_b obtained between 0 and $588 \mu\text{g mL}^{-1}$ MNPs (Fig. 5A), the expected E_d as a function of MNP concentration (Fig. 1B), and the calculated E_V obtained for the MNP-based ^{210}Po collection from ground water onto MNPs (listed in Table 4). It is noted that the optimal ranges of MNP concentrations in the scintillation cocktail must be observed (as reported in Section 4.1), or E_d will decrease, thereby negating gains in $MDA_{Bq/mL}$ achieved with increased E_V .

5.3 MNP-induced quenching

It was herein demonstrated that a modern LS analyzer can reliably measure gross α emissions from surprisingly concentrated MNP suspensions: up to 74 mg mL^{-1} and 147 mg mL^{-1} suspensions when used without and with a quench curve, respectively. The assay of even greater MNP masses can be performed by a LS analyzer if the metal oxide concentrates are first dissolved in acid, brought up in water, and added to the scintillation cocktail. In this latter example, the extreme quenching associated with the suspension of metal oxide solids was eliminated, although some quenching due to coloration of the scintillation cocktail mixture was observed. However, this quenching from dissolved MNPs was demonstrated to have inconsequential impact on instrument performance.

Quenching in LS analysis is generally attributed to three possible sources: (1) chemical, (2) optical (“color”), and (3) ionization quenching.^{26,29,68–70} Ionization quenching occurs during all α emissions; it is the result of the high density of excitation events that occur along the linear energy transfer (LET) pathway. Photon emissions are lost when concentrated ionization events occur, thus reducing the total photon output.^{26,71} Ionization quenching is the primary reason why α -emission events are binned at energy levels significantly below those of the originating emission energy in LS analyzers (*i.e.*, unquenched ^{241}Am α -emissions (5.486 MeV) are binned by the multi-channel analyzer as having a maximum channel (energy) of $\sim 800 \text{ keV}$).

However, a fourth quenching mode, self-absorption, is also possible.⁷² Self-absorption quenching is caused by the incomplete interaction of the emitted particle with the scintillation cocktail—a likely scenario for α emissions that are partially attenuated within the high density MNPs to which the source radionuclides are adsorbed, or from α particle collisions with adjacent MNPs in the cocktail suspension. The LET of α particles with emission energies close to those of ^{241}Am and ^{210}Po in the scintillation cocktail is on the order of $\sim 40 \mu\text{m}$.⁷³ Within the higher-density Fe_3O_4 , the LET distance is reduced to path-lengths of $\sim 14 \mu\text{m}$.⁷⁴ The presence of these higher density solids interspersed within the α particle trajectories can result in energy transfer into the solids, thus reducing the energy available for excitation of scintillating fluors. Optical quenching is also likely with MNP suspensions, with many of the scintillation-induced photons being absorbed or scattered by the suspended metal oxide nanoparticles.

^{||}Based on H_2O at 20°C and 1 atm; $\text{H}_2\text{O } \rho = 1.00 \text{ g cm}^{-3}$; range = $4.3 \times 10^{-3} \text{ g cm}^{-2}$.

^{**} $\text{Fe}_3\text{O}_4 \rho = 5.17 \text{ g cm}^{-3}$; estimated range = $7.4 \times 10^{-3} \text{ g cm}^{-2}$.

In both of these quenching scenarios, the total number of photons available for detection by the photomultiplier tubes (PMTs) is reduced, and the pulse height spectrum is shifted to lower bins in the multichannel analyzer. For solutions bearing high MNP concentrations in suspension, dual pulse height zones become apparent (Fig. 3 and 4). This may be evidence of both self-absorption and optical quenching phenomena occurring in the same sample. It is further speculated that the lower channel range pulse height zone is caused by self-absorption quenching, a direct result of energy attenuation from α particle collisions with nearby metal oxide particles. As the MNP concentration increases in the scintillation vessel (and thus the inter-particle distances decrease), the probability of α collisions with the metal oxides increases.

The LS samples containing faintly yellow ferric chloride from the dissolved MNPs were certainly affected by optical quenching. However, the absorption of scintillation induced photons by these dissolved ferric iron-bearing salts was negligible when compared to those observed with MNP suspensions. $C_{\max}$ channel shifts and drop in tSIE parameter were not noticeable until the ferric iron concentration reached $\sim 19 \mu\text{g mL}^{-1}$, and these shifts were minor. Furthermore, the E_d was not affected within the entire ferric iron concentration range evaluated. It should be noted that the molar extinction coefficient of ferric chloride increases with increasing concentration of chloride.⁷⁵ Therefore, solubilization of the dissolved MNP salts in HCl solutions greater than 0.1 mol L^{-1} would be expected to increase the optical quenching levels in the samples, thereby resulting in lowered tSIE values.

6. Summary & conclusions

A rapid, simple and efficient assay method which, in its simplest form, avoids the use of corrosive or toxic chemicals, many commonly consumed laboratory expendables, and laboratory infrastructure in general, is presented for the determination of gross α activity from aqueous solutions. Magnetite NPs have been shown to be effective for the sorption of two representative α -emitting radionuclides (^{241}Am and ^{210}Po) from two representative naturally occurring aqueous matrices (river and ground water). A log distribution coefficient ($\log K_d$) of 4.8 was measured for ^{241}Am on the MNPs in river water; $\log K_d$ values of 5.4 were measured for ^{210}Po on the MNPs in ground water at natural pH and pH 2. Each of these values was in good agreement with those previously reported. Following the sorption of the analyte from the liquid, the superparamagnetic properties of the metal oxide nanoparticles are leveraged to concentrate the particles from the bulk solution using NdFeB magnets. Decanting the majority of the sample volume results in a concentrated MNP suspension that contains the analyte. The ability to concentrate analytes without chemical treatment steps (*e.g.*, co-precipitations, liquid/liquid extractions or columns) represents a simple and green chemical extraction method that is especially well suited to situations that may require processing of large numbers of radionuclide-bearing samples (*i.e.*, following a nuclear or radiological event).

The measurement of the concentrated α -emitting radionuclides was further simplified and expedited since chemical treatment of the concentrated MNP suspension was avoided. The authors have demonstrated that MNP suspensions can be added directly to the scintillation cocktail for measurement by a LS analyzer. Use of analyte-sorbed MNP concentrates

facilitated significant LS analyzer signal improvement over that of unprocessed samples, as effective volumes (E_V) increase with (1) high analyte concentration factors (CF_{analyte}) and (2) increasing concentrations of analyte-sorbed MNPs in the scintillation cocktail. With further nanomaterial development, this degree of signal enhancement (*via* improved CF_{analyte} factors) may be significantly increased through application of several techniques suggested in Section 5.1.

Also demonstrated was an approach whereby the analyte-sorbed MNPs can be dissolved in acid, creating a faintly colored ferric chloride solution, and then adding that solution to the scintillation cocktail. Application of this MNP dissolution step prior to solution addition to the scintillation cocktail results in greatly reduced quenching, and therefore allows for a greater equivalent mass of MNPs to be added to the sample.

Because LS analysis relies on the production, escape, and detection of scintillation-induced photons, the analytical performance of this instrument can be diminished by processes that induce quenching in the scintillation cocktail. The addition of suspensions of solids or photon-absorbing reagents into the scintillation cocktail can produce extreme quenching, and are therefore customarily avoided by analysts. Nevertheless, the authors have demonstrated that LS analyzers are capable of providing accurate α -emission count rates even when quenching conditions are severe. The approximate upper limits of MNP suspension concentrations before analytical results would be expected to fail are reported: $74 \mu\text{g mL}^{-1}$ when not using quench correction, and $147 \mu\text{g mL}^{-1}$ when employing a quench correction curve.

A comparison of calculated minimum detectable activity concentrations ($MDA_{\text{Bq/mL}}$) between a sample aliquot added directly to the scintillation cocktail and analyte-sorbed MNPs in the cocktail was presented. Whereas MDAs from direct sample aliquots to the cocktail are driven predominantly by the data acquisition time, use of the presented MNP-based method reduces $MDA_{\text{Bq/mL}}$ as a function of two components. First, the background count rate (C_b) of the LS analyzer is reduced as the MNP concentration in the cocktail increases (thereby reducing L_d); secondly, effective volumes (E_V) effectively increase the volume of the aqueous sample being analyzed. Caution must be taken to ensure that MNP concentrations in the cocktail lie within the optimal range, or a reduction in detection efficiency (E_d) will begin to diminish the benefits gained by increased E_V .

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Fig. 1. (A) Scintillation vials containing increasing MNP concentrations suspended in the scintillation cocktail. (L to R) Vials are labeled with the MNP concentrations present ($\mu\text{g mL}^{-1}$). (B) Observed transformed spectral index of the external standard (tSIE) values (●) and mean ^{241}Am detection efficiencies (E_d) (○) across the range of MNP suspension concentrations ($\pm 1\sigma$, $n = 7$). Reference sample *sans* MNPs (not shown) yielded an E_d of 0.97 ± 0.05 cps Bq^{-1} and tSIE of 521 ± 2 .

Fig. 2.

LS analyzer reported mean ^{241}Am activities ($\pm 2\sigma$) for the range of MNP suspensions in the scintillation cocktail, as per the applied quench curve ($n = 7$). Reference sample *sans* MNPs yielded 141 ± 1 Bq ^{241}Am (not shown). Solid and dotted lines indicate independently determined mean ^{241}Am activity and 2σ error (141 ± 14 Bq), respectively.

Fig. 3. LS pulse height spectra of five solutions with increasing masses of ^{241}Am bound MNPs in a scintillation cocktail suspension (30 min counts). Labels indicate sample IDs listed in Tables 1 and 2. An unquenched ^{241}Am α -emission pulse height spectrum is shown for reference.

Fig. 4. LS pulse height spectra of four solutions containing increasing masses of ²¹⁰Po-bound MNPs in scintillation cocktail suspensions. Labels indicate sample IDs listed in Tables 4 and 5. Peak labeled “No MNPs” is a direct aliquot (2.0 mL) of the ²¹⁰Po-spiked HGW sampled prior to MNP addition.

Fig. 5. (A) Observed reduction in the background count rate (C_b) as a function of MNP concentration in the scintillation cocktail. (B) Calculated MDA concentrations ($\text{MDA}_{\text{Bq/mL}}$) expressed as a function of data acquisition time. Dashed line shows MDA concentration for 2.0 mL aqueous sample added directly to the scintillation cocktail. Legend lists analyte-sorbed MNP concentrations in the cocktail ($\mu\text{g mL}^{-1}$); MNP concentrations correspond to samples F–I in Table 4.

Table 1Counting conditions for LS analysis of ^{241}Am sorbed onto MNPs^a

Sample ID	V_{CMNP} , mL	MNP mass, μg	Conc. in the LS cocktail, mg mL^{-1}		E_V^e , mL	^{241}Am present, Bq
			MNP suspension ^b	Dissolved MNPs ^{c,d}		
A	0.04	18.3	1.08	0.76	0.16 ± 0.01	6.1 ± 0.4
B	0.10	45.8	2.69	1.91	0.40 ± 0.03	15.3 ± 1.1
C	0.40	183	10.8	7.63	1.59 ± 0.14	61.4 ± 4.4
D	1.0	458	26.9	19.1	3.98 ± 0.35	153 ± 11
E	2.0	916	53.9	38.2	7.97 ± 0.69	307 ± 22

^aThe concentrated suspension of radionuclide-loaded MNPs (CMNP) contained 0.458 mg mL^{-1} with $335 \pm 24 \text{ Bq mg}^{-1}$ ^{241}Am .^b15 mL LS cocktail + 2.0 mL (MNP suspension + water).^cMNPs dissolved in HCl followed by transfer of evaporated salts to plastic LSC vials (15 mL cocktail) using 2 mL 0.1 M HCl.^dValues are Fe concentration based on the Fe fraction in Fe_3O_4 NPs determined at $0.708 \pm 0.006 \text{ g g}^{-1}$.^ePer eqn (3), where $\text{CF}_{\text{analyte}}$ is $8.70 \pm 0.76 \text{ mL mg}^{-1}$; V_{CMNP} and CMNP listed in this table.

Table 2
LS counting results for ^{241}Am *via* the MNP suspension and dissolved MNPs. See Table 1 for LS sample preparation details^a

Sample ID	MNP suspensions				Dissolved MNPs			
	C _{max} channel ^b	tSIE ^b	R _{mean} cps	Mass corr. count rate, cps mg ⁻¹	C _{max} channel ^b	tSIE ^b	R _{mean} cps	Mass corr. count rate, cps mg ⁻¹
A	613	499	5.68 ± 0.06	310.3 ± 3.1	552	480	5.86 ± 0.06	319.9 ± 3.1
B	548	452	14.8 ± 0.1	323.1 ± 2.0	545	475	^c	^c
C	380	313	59.2 ± 0.2	323.2 ± 1.0	547	475	58.9 ± 0.2	321.4 ± 1.0
D	253	205	152.5 ± 0.3	332.9 ± 0.6	480	426	149.0 ± 0.3	325.3 ± 0.6
E	170	147	290.4 ± 0.4	317.1 ± 0.4	494	427	292.8 ± 0.4	319.6 ± 0.4
			Mean ± 1σ = 321 ± 9				Mean ± 1σ = 322 ± 3	

^aCount rate errors expressed as $\pm 1\sigma$ of the mean.

^bThe ^{241}Am reference standard *sans* MNPs yielded a C_{max} channel at 643, with a tSIE of 520 ± 10 ($n = 3$).

^cNo result; some loss of analyte occurred during dissolution and vessel transfer.

Table 3

Calculated activity concentrations of ^{241}Am in river water based on the assay of MNP suspensions and dissolved MNPs in the scintillation cocktail^a

Sample ID	MNP suspensions		Dissolved MNPs	
	$A_{\text{sample}}, \text{Bq mL}^{-1}$	Bias, ^b %	$A_{\text{sample}}, \text{Bq mL}^{-1}$	Bias, ^b %
A	36.8 ± 3.7	-4.5	37.9 ± 3.9	-1.5
B	38.3 ± 3.9	-0.5	–	–
C	38.3 ± 3.9	-0.5	38.1 ± 3.9	-1.0
D	37.6 ± 3.8	+2.4	38.6 ± 3.9	+0.2
E	37.6 ± 3.8	-0.5	37.9 ± 3.8	-1.6

^a Per eqn (2), where R_{meas} is provided in Table 2, E_V provided in Table 1, and $E_d = 0.97 \pm 0.05 \text{ Bq mL}^{-1}$.

^b Based on the independently determined ^{241}Am activity concentration of $38.5 \pm 1.9 \text{ Bq mL}^{-1}$.

Table 4

Counting conditions for LS analysis of ^{210}Po sorbed onto MNPs in ground water at pH ~8 and ~2

pH	Sample ID	V_{CMNP} , mL	MNP mass, ^a mg	MNP conc. in the LS Cocktail, ^b mg mL ⁻¹	E_V , ^c mL	^{210}Po present, ^d Bq
8.3	F	0.5	0.555	32.6	5.5 ± 0.1	44.5 ± 0.6
	G	1.0	1.11	65.3	11.1 ± 0.2	89.0 ± 1.2
	H	1.5	1.66	97.9	16.6 ± 0.3	133.5 ± 1.9
	I	2.0	2.22	131	22.2 ± 0.5	178.1 ± 2.5
2.0	J	0.5	0.518	30.4	5.4 ± 0.2	46.9 ± 1.2
	K	1.0	1.04	60.9	10.9 ± 0.4	93.9 ± 2.4
	L	1.5	1.55	91.3	16.3 ± 0.6	140.8 ± 3.6
	M	2.0	2.07	122	21.7 ± 0.8	187.7 ± 4.8

^aSet F-I: $C_{\text{MNP}} = 1.109 \text{ mg mL}^{-1}$; set J-M: $C_{\text{MNP}} = 1.035 \text{ mg mL}^{-1}$.

^b15 mL LS cocktail + 2.0 mL (MNP suspension + water).

^cPer eqn (3), where CF_{analyte} is $10.0 \pm 0.2 \text{ mL mg}^{-1}$ (samples F-I) and $10.5 \pm 0.4 \text{ mL mg}^{-1}$ (samples J-M); V_{CMNP} and C_{MNP} listed in this table.

^dBased on independently determined ^{210}Po activity on MNPs; set F-I = $80.2 \pm 1.1 \text{ Bq mg}^{-1}$; set J-M = $90.7 \pm 2.3 \text{ Bq mg}^{-1}$.

Table 5

LS analysis results for ^{210}Po sorbed onto MNPs concentrated from ground water at natural pH and at pH 2.0. See Table 4 for LS sample preparation details^a

pH	Sample ID	C_{max} channel ^b	tSIE ^b	A_{meas} ^c , Bq	Mass corr. activity, Bq mg ⁻¹	A_{sample} ^d , Bq mL ⁻¹
8.3	F	166	155 ± 4	42.8 ± 0.3	77.2 ± 0.5	7.72 ± 0.16
	G	81	96 ± 4	86.0 ± 1.1	77.5 ± 1.0	7.75 ± 0.18
	H	42	73 ± 4	135.7 ± 3.0	81.5 ± 1.8	8.15 ± 0.24
	I	24	61 ± 4	174.7 ± 3.8	78.7 ± 1.7	7.87 ± 0.23
				Mean ± 1σ =	79 ± 2	7.9 ± 0.2
2.0	J	162	154 ± 4	44.3 ± 0.2	85.7 ± 0.4	8.16 ± 0.31
	K	87	98 ± 3	88.5 ± 1.1	85.5 ± 1.1	8.14 ± 0.33
	L	48	77 ± 3	138.7 ± 4.3	89.3 ± 2.8	8.51 ± 0.42
	M	24	63 ± 3	180.0 ± 4.9	86.9 ± 2.4	8.28 ± 0.39
				Mean ± 1σ =	87 ± 2	8.3 ± 0.2

^aActivity errors expressed as ±1σ of the mean.

^bFor comparison, a ^{210}Po reference standard *szns* nanoparticles yielded a C_{max} channel of 553 and tSIE of 525 ± 2 ($n = 7$).

^cAnalysis performed using the quench curve generated from ^{241}Am spikes into MNP/scintillation cocktail suspensions.

^dPer eqn (2), wherein EV is provided in Table 4 and A_{meas} is provided here.