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Determination of ^{36}Cl in Nuclear Waste from Reactor Decommissioning

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An analytical method for the determination of ^{36}Cl in nuclear waste such as graphite, heavy concrete, steel, aluminum, and lead was developed. Several methods were investigated for decomposing the samples. AgCl precipitation was used to separate ^{36}Cl from the matrix elements, followed by ion-exchange chromatography to remove interfering radionuclides. The purified ^{36}Cl was then measured by liquid scintillation counting. The chemical yield of chlorine, as measured by ICPMS, is above 70% and the decontamination factors for all interfering radionuclides are greater than 10^6. The detection limit of this analytical method for ^{36}Cl is 14 mBq. The method has been used to determine ^{36}Cl in heavy concrete, aluminum, and graphite from the Danish DR-2 research reactor.

The importance of ^{36}Cl in geology, the environment, and radioactive waste management results from its long half-life ($T_{1/2} = 3.01 \times 10^5$ years), origins both natural and anthropogenic, high β energy (708.6 keV), and high mobility in the environment.[1] In nature, ^{36}Cl is produced mainly by cosmic ray nuclear reactions involving argon isotopes in the atmosphere, spallation reactions in the upper layer of the lithosphere, and thermal neutron reactions of ^{35}Cl in the hydrosphere.[2−5]

However, most of the ^{36}Cl now present in the environment has been produced by human activities since the 1950s. Nuclear weapons testing has released large amounts of ^{36}Cl into the atmosphere and oceans, and this has subsequently spread all over the world.[6,7] Even larger amounts of ^{36}Cl are produced in nuclear reactors by the neutron activation reaction ^{35}Cl(n, γ)^{36}Cl, due to the presence of chlorine in fuel elements, graphite, cooling water, and construction materials such as steel and concrete. Most of the ^{36}Cl produced in nuclear reactors remains inside the materials from which it is formed, and only a small proportion is released into the environment.

In decommissioning nuclear facilities, the radioactive inventory of various materials needs to be assessed for the classification and repository of nuclear waste. Apart from the reactor core, most of the radioactivity in a closed reactor presents in the moderators, such as graphite and water, and the construction materials.

The radioactivity of irradiated reactor materials comes from nuclides such as ^{3}H, ^{14}C, ^{36}Cl, ^{41}Ca, ^{55}Fe, ^{60}Co, ^{63}Ni, ^{90}Sr, ^{133}Ba, ^{137}Cs, ^{152}Eu, ^{154}Eu, and some transuranics.[8] Of these, the γ emitters such as ^{60}Co, ^{152}Eu, ^{154}Eu, ^{133}Ba, and ^{137}Cs can be easily determined by γ spectrometry. However, the determination of β and α emitters, such as ^{3}H, ^{14}C, ^{36}Cl, ^{41}Ca, ^{63}Ni, ^{55}Fe, ^{90}Sr, and the α-emitting transuranics, is more difficult. The poor energy resolution of β spectroscopy, and the high self-absorption of α particles in the samples, mean that these radionuclides must be completely separated from their matrixes, and from other radionuclides, before their activity can be determined.

Analytical methods for ^{3}H, ^{14}C, ^{41}Ca, ^{63}Ni, ^{55}Fe, and ^{90}Sr in concrete and graphite have been developed in our laboratory.[9−11] The present work aims to develop an accurate, sensitive, and simple radiochemical analytical method for the determination of ^{36}Cl in graphite and construction materials.

As mentioned above, most of the ^{36}Cl in nuclear reactors comes from the reaction ^{35}Cl(n, γ)^{36}Cl. ^{36}Cl is also produced by other two nuclear reactions—^{39}K(n, α)^{36}Cl, and ^{34}S(n, γ)^{35}S (β^-)^{35}Cl(n, γ)^{36}Cl—but the low neutron reaction cross section of ^{39}K and the low isotopic abundance of ^{34}S ensure that, for most reactor materials, the ^{35}Cl(n, γ)^{36}Cl reaction dominates.

^{36}Cl is a pure β emitter, which decays by emitting β particles ($E_{max} = 708.6$ keV, 98.1%) and by electron capture (1.9%). It can therefore be detected by β counting methods such as liquid scintil-

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lation counting (LSC)[12-19] and accelerator mass spectrometry.[20-24] In this work, LSC is used for the detection of ^{36}Cl.

Nuclear waste contains many different radionuclides, some of which, such as ^3H, ^{14}C, ^{152}Eu, ^{154}Eu, ^{60}Co, ^{55}Fe, and ^{133}Ba, are highly active in the first few years after reactor operation has stopped. Determining ^{36}Cl therefore requires a chemical separation method with a high decontamination factor. Many chemical separation procedures for the determination of ^{36}Cl have been reported previously. Most of these rely on volatilizing chlorine at high temperatures, followed by precipitating AgCl, and dissolving the precipitate with ammonium.[12-19]

Nuclear reactors generally contain large volumes of graphite and heavy concrete (concrete containing barium sulfate), which contribute considerable amounts of low- and intermediate-level radioactive waste. Calculations of radionuclide inventories in the Danish DR2 reactor, for instance, have shown that graphite was the main source of radioactivity at time of dismantling.[25] Steel and other metals such as aluminum and lead are also used extensively in nuclear reactors, and ^{36}Cl will also be produced from the chlorine present as an impurity in these materials.[26] Reactor water also contains ^{36}Cl, some from the chlorine present as an impurity in the water and the rest leached from the reactor materials.[27] High ^{36}Cl activity has also been found in ion-exchange resins, which concentrate ^{36}Cl from the reactor water.[16-18]

Analytical methods reported for the determination of ^{36}Cl have focused on ion-exchange resins, evaporator concentrates, concrete and water from nuclear facilities,[12-19] and biological and environmental samples such as soil, lichens, bones, and water.[2,20-24] A few methods have been reported for determining ^{36}Cl in graphite,[18,19] but it has not been possible to reproduce these to obtain reliable results. No method has been reported for the determination of ^{36}Cl in steel, aluminum, lead, and heavy concrete. Graphite is difficult to dissolve because it resists concentrated acids and bases, even at high temperatures. Heavy concrete, which is used as a shielding material due to high absorption of radiation, consists mainly of Ba_2SO_4 and silicates. The standard acid digestion with HF cannot be used for the decomposition of heavy concrete.

This work presents a method for determining ^{36}Cl based on the decomposition of steel, lead, aluminum, graphite, and heavy concrete to release chlorine, followed by separation of ^{36}Cl from the matrix, and purification to remove other radionuclides.

EXPERIMENTAL SECTION

Equipment and Chemicals. A Quantulus 1220 liquid scintillation counter (Perkin-Elmer Inc., Turku, Finland) was used to measure ^{36}Cl. A high-purity germanium detector with Genie 2000 γ spectroscopy analysis software (Canberra Industries) was used to acquire and analyze γ spectra. Inductively coupled plasma mass spectrometry (ICPMS; PlasmaTrace2, Micromass, Manchester, UK) was used to determine stable chlorine. Ultima Gold LLT (Perkin-Elmer Inc., Groningen, The Netherlands) was used as scintillation cocktails. ^{36}Cl standard solution (NIST-SRM-4943) was purchased from the National Institute of Standard and Technology (Gaithersburg, MD 20899). ^3H, ^{14}C, ^{125}I, ^{137}Cs, ^{60}Co, ^{152}Eu, ^{85}Sr, and ^{133}Ba tracers were supplied by the isotope group at Risø National Laboratory. Bio-Rad anion-exchange resin (AG1 × 4, 50–100 mesh, Cl^- form) was purchased from the Bio-Rad Laboratory. Other reagents used were analytical-grade.

Sampling and Sample Preparation. Eight graphite samples were collected from the thermal column of the Danish DR-2 research reactor. To avoid contamination, the surface material was not collected. A flat 16-mm drill was used to collect samples in the form of fine powder ($d < 0.2$ mm), and a subsample weighing 5–10 g was taken from each sample.

Six samples of heavy concrete were collected from a core drilled in 2002 from the DR-2 biological shield. The core is ~2 m long, representing the concrete thickness from 1085 to 3065 mm as measured from the reactor core and is 34.2 mm in diameter. Slices ~10 mm thick were cut from the core. The samples were ground to fine powder ($d < 0.2$ mm) for analysis.

At the inner end of the drilled core are a 10-mm thickness of aluminum (the reactor tank, samples referred to as B1 in this work), 60 mm of lead (B2 sample), and 10 mm of aluminum (B4 sample). The aluminum and lead samples were cut into small pieces for analysis; detailed information on the sampling technique has been reported elsewhere.[11]

A stainless steel screw taken from the DR-2 reactor was cut into small pieces for analysis. Two inactive stainless steel samples in chip form—AISI316 (NIST-SRM-160b) and AISI348 (NIST-SRM 123c)—were used to investigate the separation of chlorine from steel.

Sample Decomposition. (1) Decomposition of Graphite, Stainless Steel, Aluminum, and Lead by Acid Digestion. For the digestion of graphite, ~0.2 g of graphite sample was weighed into a three-necked flask connected to a digestion system (Figure 1). Fifty milligrams of Cl carrier (NaCl or $NaClO_3$) and 2–5 mg of Eu, Fe, Co, Ni, and I hold-back carriers were added, followed by 20 mL of a mixture of concentrated acids (H_2SO_4:HNO_3:$HClO_4$ = 15:4:1).

Nitrogen was then bubbled slowly through the solution, and the sample was heated to 150–200 °C and maintained at this temperature until a clear solution was obtained (1–1.5 h). On completion, the adsorption solutions in the wash bottles (9 and

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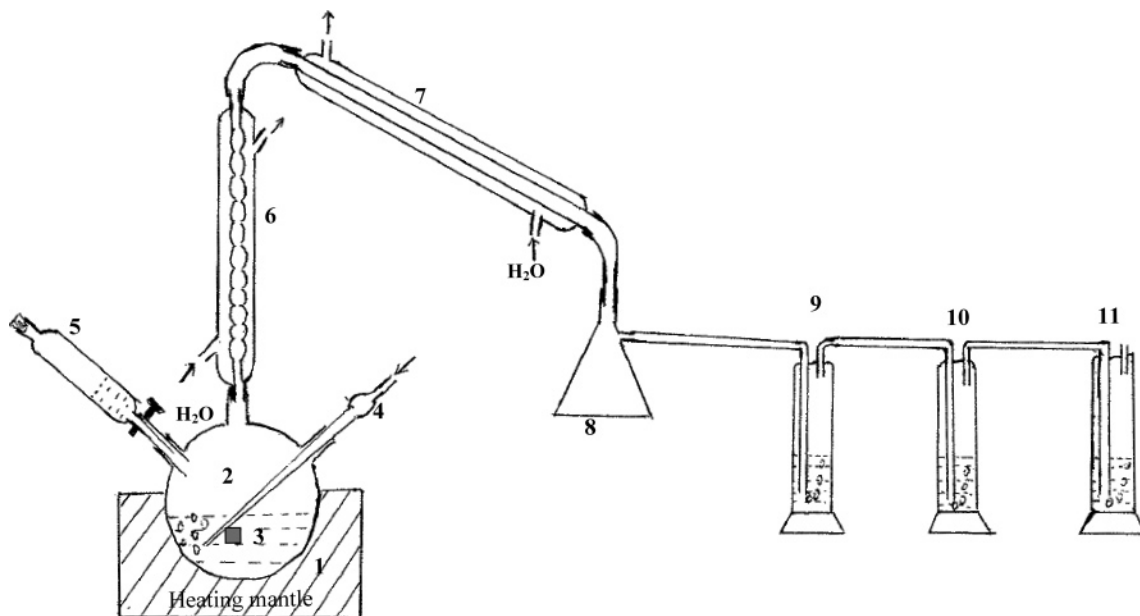
Figure 1. Acid digestion system for the decomposition of graphite, steel, aluminum and lead samples. Key: 1, Heating mantle; 2, three-necked flask; 3, sample in acid mixture; 4, bubbling tube; 5, separating funnel for adding acids; 6, 7, reflux condenser; 8, receiver; 9, wash bottle containing water; 10, 11, absorption bottles containing 0.4 mol/L NaOH.

10 in Figure 1) were combined to yield a ^{36}Cl solution for subsequent purification.

For the metals, 0.2−1 g of steel or aluminum, or 5 g of lead, was weighed into the three-neck flask (Figure 1). Fifty milligrams of stable Cl carrier and 2−5 mg of Eu, Fe, Co, Ni, and I hold-back carrier were added, followed by 25 mL of H$_2$O, 25 mL of H$_2$SO$_4$, and 3 mL of H$_3$PO$_4$ for steel samples; 30 mL of 5 mol/L H$_2$SO$_4$ for aluminum; or 30 mL of 5 mol/L HNO$_3$ for lead. Without nitrogen bubbling, the sample was then heated until all the metal dissolved. In the case of steel, this required the solution to be heated at 150−200 °C for 1.5−2 h; for aluminum and lead, the solution was heated at 70−90 °C for 0.5−1 h. Once all the metal had been dissolved, the wash solution from the first condenser (No. 6 in Figure 1) was added to the liquid in the three-necked flask to yield a ^{36}Cl solution for subsequent purification.

(2) Decomposition of Heavy Concrete by Alkali Fusion. A 1−5-g sample of heavy concrete was weighed in a porcelain crucible; 50 mg of Cl carrier (NaCl or NaClO$_3$) and 2−5 mg of Eu, Fe, Co, Ni, and I hold-back carriers were added, and the mixture was evaporated to dryness on a hotplate. NaOH and Na$_2$CO$_3$ were added and mixed with the sample (sample:Na$_2$CO$_3$:NaOH = 1:1:3), after which the crucible was heated to 450−500 °C for 3−4 h. After the crucible had cooled to room temperature, the resulting fused cake was dissolved in hot water and the precipitate separated by centrifuging. The precipitate was washed with hot water two or three times, and the washings were added to the solution obtained by centrifuging to yield a ^{36}Cl solution for subsequent purification.

Chemical Separation of Chlorine. (1) Separation of Cl from Absorption Solution in Graphite Dissolution. The combined solution from the wash bottles was acidified to pH 2 using HNO$_3$, with stirring to release the resulting CO$_2$. This step needs to be carried out with care, because the gas contains radioactive ^{14}CO$_2$.

Two milliliters of 2 mol/L NaNO$_2$ solution was then added to reduce chlorine to chloride, followed by 4 mL of 3 mol/L AgNO$_3$ to precipitate Cl$^-$ as AgCl. The precipitate, containing AgCl and AgI, was separated by centrifuging, and then washed with 8 mol/L HNO$_3$ to remove any Ag$_2$SO$_3$ and Ag$_2$SO$_4$ that might have formed.

The 25% NH$_3$ was then added to the centrifuge tube to dissolve the AgCl, and the dissolved AgCl separated from the AgI precipitate by centrifuging again. Two-tenths of a milliliter of 3.0 mol/L AgNO$_3$ was added to the supernatant, after which the solution was acidified to pH <2 with HNO$_3$, and the AgCl precipitate separated by centrifuging and washing with water.

(2) Separation of Cl from Leachate of Alkali-Fused Concrete. The water leachate from the alkali-fused heavy concrete was acidified to pH 2 with HNO$_3$ and the solution stirred to release CO$_2$. A small amount of BaSO$_4$, which sometimes precipitated at this point, was removed by filtering through a filter paper. Two milliliters of 2 mol/L NaNO$_2$ solution was then added to the solution to reduce chlorine to chloride, followed by 1.5 mL of 3 mol/L AgNO$_3$ to precipitate Cl$^-$ as AgCl. The AgCl was purified by dissolving with NH$_3$ and reprecipitated by lowering the pH to 2 with HNO$_3$.

(3) Separation of Cl from Solution from Steel, Aluminum, and Lead Dissolution. Twenty milliliters of HNO$_3$ was added to the solution resulting from the dissolution of steel or aluminum and allowed to react for 5 min. The solution was then diluted with water by a factor of 10−15. Two milliliters of 2 mol/L NaNO$_2$ was added to reduce chlorine to chloride, followed by 1.5 mL of 3 mol/L AgNO$_3$ to precipitate Cl$^-$ as AgCl. The AgCl was then purified by the method described above.

In the case of lead, the solution resulting from the dissolution with HNO$_3$ was directly diluted with water by a factor of 10, without the addition of further HNO$_3$. A precipitate of AgCl was then prepared by the same method used for steel and aluminum above.

Chemical Purification of Cl by Anion-Exchange Chromatography. The separated AgCl was dissolved in 25% NH_3 and the solution loaded onto a Bio-Rad AG1 × 4 anion-exchange column (50–100 mesh, id. 2.0 × 25 cm for graphite and 1.0 × 15 cm for the other samples). The resin had previously been converted to the NO_3^- form and conditioned with 10 mL of 25% NH_3 solution. The 25% NH_3 was used to wash the centrifuge tube and the column until the effluent contained no Ag^+ when tested with AgCl.

Chloride on the column was then eluted with NH_4NO_4–NH_4-OH solution. The eluate was evaporated to dryness on a hotplate at 150 °C; the residue was dissolved in 2 mL of water, and the solution transferred to an LSC vial.

To investigate the removal of interfering radionuclides and the recovery of chlorine in the chemical separation procedure, tracer radioisotopes were added to inactive samples of graphite, heavy concrete, steel, aluminum, and lead, which were then digested and purified using the methods described above. The isotopes used included ^{3}H, ^{14}C, ^{125}I, ^{137}Cs, ^{60}Co, [152]Eu, [85]Sr, and [133]Ba (2–5 kBq each); [55]Fe and [63]Ni (500 Bq each), and [36]Cl (NaCl; 3 Bq).

Measurement of [36]Cl by Liquid Scintillation Counting. Samples prepared by the methods described above were mixed with Ultima Gold LLT scintillation cocktail in a 20-mL polyethylene vial. [36]Cl was then measured by an ultralow-level Wallac 1220 Quantulus liquid scintillation counter using the high-energy β-nuclide window. The sample and blank were counted for three cycles of 60 min each, and the average of the three cycles was calculated. The quench level was measured by the external standard method (SQP(E)), and the counting efficiency calculated using standards at different quench levels (Figure S-1, Supporting Information).

Measurement of Stable Chlorine by ICPMS. To calculate the yield of [36]Cl achieved by the chemical separation procedure, ICPMS was used to determine stable chlorine in samples of untreated concrete and the chlorine content of the separated samples. Before analysis, the samples were diluted with 1% (v) HNO_3 until the Cl concentration was less than 10 ppm and the total concentration of dissolved solids was less than 0.5%. The samples were spiked with 2 ppb Cs as an internal standard. A series of calibration standards from 0.1 to 10 ppm Cl in 1% HNO_3, each with 2 ppb Cs, was used for calibration.

The analysis was performed with a Plasmatrace 2 high-resolution inductively coupled plasma mass spectrometer (MicroMass) equipped with a standard conical nebulizer and a double-pass Scott-type spray chamber. Chlorine was measured at m/z 35 in medium-resolution mode (3000 resolution). The detection limit, calculated as three times the standard deviation of several blank samples, was found to be 0.01 ppm.

RESULTS AND DISCUSSION

Figure 2 shows the distribution of [36]Cl in the concrete core. For comparison, the distributions of [63]Ni and [55]Fe (measured in 2004)[11] are also shown. It is clear that the distributions of all three species are similar.

In the first 470 mm of concrete (from 1080 to 1550 mm from the reactor core), the activity of [36]Cl decreases exponentially with distance from the reactor core. From 1600 to 3000 mm, the [36]Cl concentration does not change significantly; this is in agreement with measurements of ^{3}H, ^{14}C, [41]Ca, [55]Fe, [63]Ni, and γ emitters in the concrete core.[9–11,29]
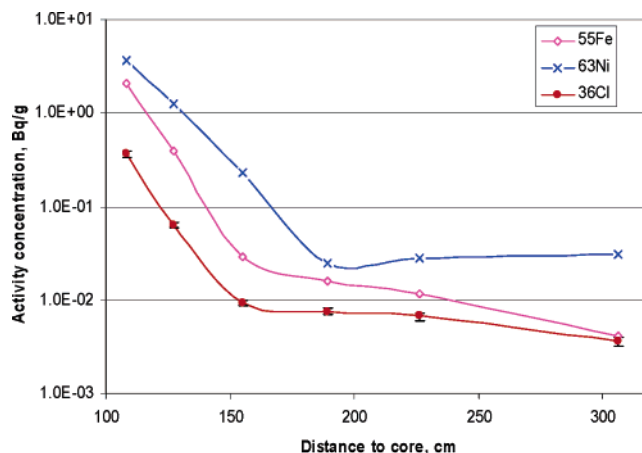
Figure 2. Distribution of [36]Cl, [55]Fe, and [63]Ni in the concrete core from Danish research reactor DR-2,[11] with error bars showing the analytical uncertainty.

Table 1. Concentrations of [36]Cl in Samples from the Graphite Thermal Column, Aluminum Tanks and Lead Shielding in the Concrete Core from the Danish DR-2 Reactor[a]

sample	code	[36]Cl, Bq/g (mean ± SD)	[63]Ni, Bq/g	[36]Cl/[63]Ni activity ratio
graphite	5.5 Yi	0.18 ± 0.03	5.76	0.030
graphite	5.5 Yy	3.58 ± 0.13	102	0.035
graphite	5.5 Ii	22.6 ± 1.5	499	0.045
graphite	5.5 Iy	6.61 ± 0.52	74.9	0.088
graphite	7.5 Yi	6.37 ± 0.48	134	0.048
graphite	7.5 Yy	5.57 ± 0.54	88.3	0.063
graphite	7.5 Ii	39.9 ± 3.4	758	0.053
graphite	G	3.33 ± 0.28	61.2	0.054
aluminum	B1	0.027 ± 0.003	15.6	0.0017
aluminum	B2	0.023 ± 0.003	15.5	0.0015
lead	B4	0.0032 ± 0.0012	2.58	0.0012

[a] The values of the mean and standard deviation for [36]Cl activity refer to three aliquots of sample. The results are compared with [63]Ni activity in the same samples.[11]

The exponential parts of the curves indicate that very few neutrons penetrate further than 1000 mm into the concrete shield, which spans the range 1080–3000 mm from the reactor core. The flat part of the curves in Figure 2 is probably due to contamination during sampling. On this basis, at least 60% of the concrete (2000–3000 mm from the reactor core) can be treated as nonradioactive waste.

The Danish DR-2 reactor operated from 1959 to 1975. Brodersen[29] calculated the average neutron flux at the inner face of the concrete core (1080 mm from the reactor core) to be 6.7 × 10^{8} neutrons cm^{-2} s^{-1} during the 16 years of irradiation. Using this average neutron flux and the measured concentrations of stable Cl in the DR-2 concrete of 48.4 ± 4.1 $\mu g/g$, as well as other parameters listed in Table S-1 for the reaction [35]Cl(n, γ)[36]Cl, the corresponding [36]Cl activity concentration can be calculated as 0.668 Bq/g. This is in reasonable agreement with the measured value of 0.37 Bq/g (Figure 2).

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Table 2. Recovery of Chlorine in the Chemical Separation Procedure Measured from Stable Chlorine and ^{36}Cl Tracer^a

| graphite, g | form | stable chlorine | | | ^{36}Cl tracer | | |
		Cl, mg	measd, mg	recovery, %	added, Bq	measd, Bq	recovery, %
0.210	NaCl	50	315.5	87.4	2.50	2.17	86.8
0.255	NaCl	50	368.9	92.3	2.50	2.13	91.2
0.195	NaClO$_3$	50	297.2	89.8	2.50	2.18	89.2
0.301	NaClO$_3$	50	305.7	96.5	2.50	2.20	97.0

^{a} Inactive graphite was used.

Although heavy concrete contains much more potassium and sulfur than chlorine, the contributions of these elements to the total amount of ^{36}Cl in concrete are negligible. As far as potassium is concerned, ^{36}Cl is produced by the fast neutron reaction ^{39}K(n, α)^{36}Cl. The fast neutron flux in the concrete core is unknown, if it is assumed to have the same value as the thermal neutron flux. The concentration of K in concrete has been reported to be ~7.5 mg/g.[8] With these assumptions, the calculated ^{36}Cl contribution from potassium is only 2.8% of that from stable chlorine.

The heavy concrete used in the DR-2 reactor contains 9.8% Portland cement and 87.6% Barite (BaSO$_4$), so the concentration of sulfur is very high (118 mg/g).[31] The reaction ^{34}S(n, γ)^{35}S(β^-)^{35}Cl(n, γ)^{36}Cl, however, can be calculated to contribute only 0.0024% to the total ^{36}Cl.

Table 1 shows the concentrations of ^{36}Cl in graphite samples from the DR-2 reactor. They are much higher than those in the concrete, which can be attributed to the high neutron flux in the graphite thermal column. The estimated integrated neutron flux in these graphite stringers is $(0.65-1.79) \times 10^{20}$ neutrons cm^{-2}, or an average neutron flux of $(2.06-5.68) \times 10^{12}$ neutrons cm^{-2} s^{-1} over the 16 years of irradiation[30]—~4 orders of magnitude higher than at the inner face of the concrete core.

The concentration of stable Cl in the graphite has not been determined. Graphite used in nuclear reactors is normally treated with gaseous chlorine at high temperature to remove boron, a neutron absorber, by converting it to volatile boron trichloride.[27] As a result of this treatment, the graphite may contain residual chlorine, although the amount is likely to be small due to the high temperatures used. The reported chlorine concentration in graphite used as a reflector in nuclear reactors ranges from 0.8 to 8.8 ppm.[27] Assuming a Cl concentration of 1 ppm, the ^{36}Cl activity concentration in graphite can be calculated as 43−119 Bq/g, which is comparable to the highest measured value of 39.9 Bq/g.

Table 1 shows the ^{36}Cl analytical results for two aluminum samples and one lead sample from the concrete core. The concentrations of ^{36}Cl in the aluminum are higher than in the lead by a factor of 8, a result similar to that shown by ^{63}Ni and ^{55}Fe. This may be due to the different concentrations of stable Cl, Fe, and Ni in the two materials.[11] Table 1 also lists the concentration of ^{63}Ni in graphite, aluminum, and lead; the calculated ^{36}Cl/^{63}Ni activity ratios are 0.03−0.09 for graphite and 0.0012−0.0017 for aluminum and lead. The variability of the ^{36}Cl/^{63}Ni ratio in graphite

may result from inhomogeneous distribution of Cl and Ni. The fact that the ^{36}Cl/^{63}Ni ratio in aluminum and lead is 20 times lower than in graphite can be attributed to the higher concentration of Cl in graphite than in aluminum and lead.

One stainless steel sample taken from the DR-2 reactor was analyzed for ^{36}Cl, ^{55}Fe, and ^{63}Ni. A very low concentration (0.10 Bq/g) of ^{36}Cl was found, compared to 150 kBq/g for ^{63}Ni and 1.42 MBq/g (decay corrected to 1975, when the reactor was decommissioned) for ^{55}Fe; this should attributed to the very low concentration of stable chlorine in the steel.

No Cl concentration was determined in this steel sample. Parry et al.[26] tried to determine Cl in steel samples using radiochemical neutron activation analysis, but found that the concentration of Cl in all six kinds of steel tested was below the detection limit (0.1−1.8 mg/kg). The concentrations of Ni and Fe in the steel samples were estimated to be 12 and 45%, respectively. Based on these data, and the 16-year operating period of the DR-2 reactor, the concentration of stable chlorine in the investigated steel sample can be estimated at 0.20 mg/kg. This suggests that ^{36}Cl does not contribute significantly to the radioactivity of the stainless steel sample investigated in this work.

Separation of ^{36}Cl from Stainless Steel. Stainless steel is used extensively in nuclear reactors as a construction material and may be exposed to high neutron fluxes. Although the concentration of chlorine in the steel samples investigated here was very low, much higher chlorine concentrations (50−130 mg/kg) have been estimated in some steels, such as type 304L stainless steel.[8] In such cases, ^{36}Cl would be one of the main long-lived radionuclides in the irradiated stainless steel, so the determination of ^{36}Cl in stainless steel will be important in reactor decommissioning and waste disposal. However, no report on the analysis of steel for ^{36}Cl is available.

The methods normally used to dissolve stainless steel involve the addition of large amounts of chlorine, either as HCl or as chloride used with HNO$_3$. It has been reported that to dissolve 0.7 g of stainless steel required 17.3 g of Cl as HCl; dissolution with KCl and HNO$_3$ significantly reduced the amount of Cl needed, but the figure was still 1.0 g of Cl as KCl.[26] The addition of such large amounts of Cl will make the further separation of Cl by anion-exchange chromatography more difficult, requiring a large column and a large volume of eluent. The large amount of Cl and NH$_4$-NO$_3$ in the eluate would also need a large volume of cocktail to produce a clear solution for counting, and this would raise the detection limit for ^{36}Cl.

(31) Ølgaard, P. L. Decommissioning of research reactor experience from the DR-2, Risø-I-1166; Risø National Laboratory: Roskilde, Denmark, 1997.

Table 3. Recovery of Cl and Decontamination Factors for Other Elements and Radionuclides in the Chemical Separation Procedure

element	AgCl precipitation	anion exchange	whole procedure
Cl (recovery, %)	96.5	98.3	94.7 ± 3.2
I (^{125}I)	1.4×10^3	5.4×10^3	2.9×10^6
S	1.5×10^3		5.6×10^6
tritium	2.1×10^3		4.8×10^6
^{14}C (CO_3^{2-})	1.5×10^3		2.8×10^6
Co (^{60}Co)	1.9×10^3	8.5×10^3	8.5×10^6
Eu (^{152}Eu)	4.7×10^3	6.5×10^3	9.9×10^6
Cs (^{137}Cs)	3.8×10^3	5.1×10^3	7.9×10^6
Ba (^{133}Ba)	6.7×10^3	4.9×10^3	5.6×10^6
Sr (^{85}Sr)	4.7×10^3	8.3×10^3	8.7×10^6
Ni (^{63}Ni)	5.9×10^3	9.8×10^3	9.8×10^6
Fe (^{55}Fe)	1.9×10^3	8.8×10^3	8.1×10^6

Stainless steel is harder to dissolve in other acids, but at high temperatures, it will be dissolved in dilute H_2SO_4. Adding H_3PO_4 can help; this may relate to the formation of complexes of Fe and other metals with H_3PO_4, so that more free H_2SO_4 is released to react with the steel. This work used a mixture of H_2SO_4 and H_3PO_4 (sample: $H_2SO_4:H_3PO_4 = 1:40:4$). By heating at 150−200 °C, stainless steel can be completely dissolved in 1.5−2 h. The solution contained a small amount of black residue (<0.03 g from 1 g of steel) that does not dissolve even in HCl or HCl + HNO_3. This was also observed by other authors.[22]

It has been reported that chlorine can be released as Cl_2 from the digestion solution by adding $KMnO_4$,[14] but our experiment showed that adding $KMnO_4$ to the H_2SO_4 made the dissolution of steel very slow and incomplete. In addition, adding $KMnO_4$ to the solution once digestion of the steel was complete released only 50−60% of the chlorine immediately; a further 3−4 h was required to release the rest of the chlorine. For these reasons, no $KMnO_4$ was used in this work.

Instead, after digestion, chlorine as HCl in the solution and on the walls of the condenser was combined and separated by AgCl precipitation, with a chemical yield of 75−85%. A small loss of Cl results from the high concentration of H_2SO_4, and from the production of H_2SO_3, which can also form precipitates with Ag^+ and interfere with the separation of Cl.

Separation of ^{36}Cl from Graphite. Chlorine exists in the graphite as an impurity; it may be separated from the graphite by acid leaching[18] or by complete decomposition of the graphite.[19] Acid leaching with HNO_3 is easy to do and simplifies the further separation of Cl, but may not release all the Cl from the graphite matrix. Two graphite samples (7.5 and 5.5 Ii in Table 1) were analyzed by both methods, and the results showed that the ^{36}Cl concentration obtained by acid leaching was only 55−70% of the value obtained by decomposition with mixed acids. The decomposition procedure is therefore more reliable.

Two methods can be used for the decomposition of graphite: ashing at high temperature or dissolution with a mixture of acids. In this work, dissolution with a mixture of H_2SO_4, HNO_3, and $HClO_4$ was used. $HClO_4$ is an important oxidizer in the decomposition of graphite; the ratio of $HClO_4$ (70%) to graphite should be higher than 3.2:1 (mL/g) or 2:1 (mol/mol). During the decomposition, carbon is oxidized to CO_2 by $HClO_4$, while $HClO_4$ is reduced to Cl^- or Cl_2, and Cl^- may also be oxidized to Cl_2. The

Cl_2 formed is released from the solution. In addition, Cl will also be released as HCl when the concentrated acids are heated. The HCl and Cl_2 released are absorbed in water in the first absorption bottle (9 in Figure 1). Some Cl was also found in the first NaOH absorption bottle (10 in Figure 1), presumably because of incomplete absorption in the first bottle. The chlorine in the NaOH absorption solution may exist as Cl^- and ClO^-, if Cl_2 is formed and absorbed in the solution.

The absorption solution was acidified with dilute HNO_3, and Ag^+ was added to precipitate Cl^-; after separation of AgCl by centrifuging, $NaNO_2$ was added to the supernatant, followed by Ag^+. No more AgCl precipitate was found in the supernatant, indicating that all the chlorine was released and absorbed in the solution as HCl, because ClO^- or ClO_3^- are easily reduced to Cl^- by $NaNO_2$ in acid solution. The reason for this may be the reduction of Cl_2 or other chlorine species (except ClO_4^-) by NO_2 (or NO_2^-) produced in the solution by the decomposition of HNO_3.

An AgCl precipitation test showed that the reaction solution contained no Cl^-. This indicates that all the chlorine was released as HCl gas from the solution during heating, while H_2SO_4 (bp 310 °C) and $HClO_4$ (bp 198 °C) were retained. No Cl was found in the second NaOH absorption bottle, which implies no loss of Cl from the digestion system. In addition, no Cl was found on the walls of the two condensers.

Because no suitable radioactive tracer is available to monitor the chlorine recovery, stable chlorine was used for this purpose instead. The graphite contains very little chlorine, so 50 mg of Cl (as NaCl or $NaClO_3$) was added to the solution as a carrier before digestion. The chlorine absorbed in the washing solution comes not only from this added Cl but also from the decomposition of $HClO_4$ during the digestion: $2C + HClO_4 = 2CO_2 + HCl$.

^{36}Cl was added to nonactive graphite to monitor the recovery. Table 2 compares the recovery obtained on one hand by stable chlorine measured using ICPMS, and on the other by ^{36}Cl tracer. The results indicate that the two methods agree very well.

Separation of Cl from Heavy Concrete. As with graphite, both acid leaching and decomposition have been used to release chlorine from the concrete matrix.[13,14] Ashton et al.[13] leached concrete with 8 mol/L HNO_3, and their analysis for synthesized concrete showed good agreement between the measured value and the amount of chlorine added. The chlorine was added to the synthesized concrete as NaCl, however, so it exists as Cl^- on the surface of the crystals and particles that make up the concrete, rather than inside them. It is therefore risky to use synthesized concrete to represent real concrete.

Because the main components of heavy concrete are $BaSO_4$ and silicates, acid digestion using HF will not decompose the material completely. Instead, pyrohydrolysis and alkali fusion are suitable methods for the complete separation of chlorine from heavy concrete. During alkali fusion, $BaSO_4$ is converted to soluble Na_2SO_4 and insoluble $BaCO_3$, while insoluble silicate is converted to soluble sodium silicate. To release chlorine, the fused cake is leached with water. Na_2CO_3 fusion[14] needs high temperatures (>900 °C), however, so chlorine is likely to evaporate from the sample before the leaching step.[27] Our experiment showed low recoveries (65−75%) using $NaCO_3$ fusion at 950 °C, compared to 80−90% recovery with NaOH−Na_2CO_3 fusion at 500 °C. Alkali
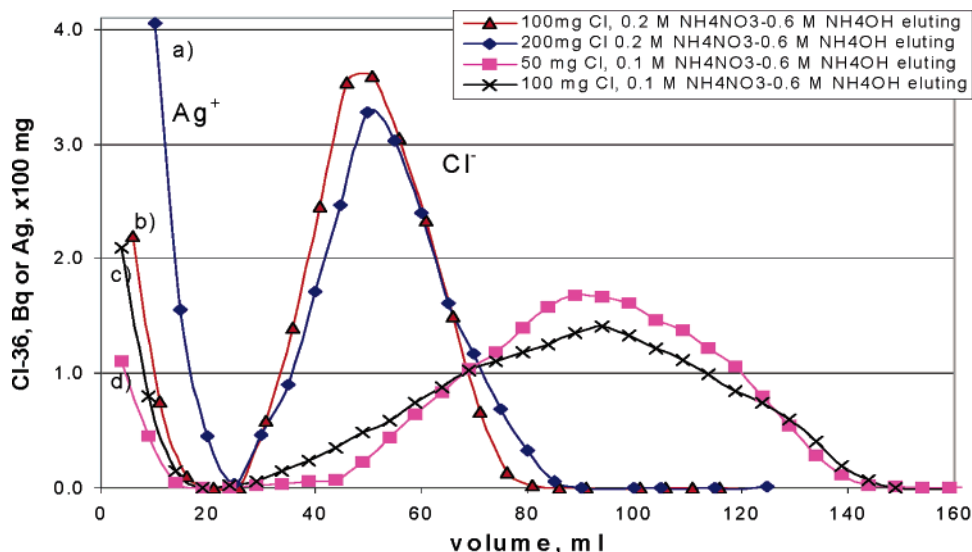
Figure 3. Separation of Ag^+ and Cl^- in anion-exchange chromatography. (a) 200 mg of Cl and 608 mg of Ag^+ are loaded, 0−10 mL is effluent, 11−25 mL is 25% NH_3 wash, and 26−130 mL is eluate of 0.2 mol/L NH_4NO_3−0.6 mol/L NH_4OH. (b) 100 mg of Cl and 304 mg of Ag^+ are loaded, 0−6 mL is effluent, 7−22 mL is 25% NH_3 wash, and 23−130 mL is eluate of 0.2 mol/L NH_4NO_3−0.6 mol/L NH_4OH. (c) 100 mg of Cl and 304 mg of Ag^+ are loaded, 0−6 mL is effluent, 17−22 mL is 25% NH_3 wash, and 23−160 mL is eluate of 0.2 mol/L NH_4NO_3−0.6 mol/L NH_4OH. (d) 50 mg of Cl and 152 mg of Ag^+ are loaded, 0−4 mL is effluent, 5−20 mL is 25% NH_3 wash, and 21−160 mL is eluate of 0.2 mol/L NH_4NO_3−0.6 mol/L NH_4OH.

fusion using $NaOH$−Na_2CO_3 at 500 °C was therefore used for the decomposition of heavy concrete.

Separation of Cl from the Main Matrix Elements Using AgCl Precipitate. Chlorine can easily be separated from most elements, except iodine, bromine, and sulfur, by AgCl precipitation. The long-lived ^{129}I (15.7×10^6 years) is likely to be the main interfering radionuclide in the determination of ^{36}Cl if it is present in comparable concentration.

If ^{129}I needs to be measured, iodine can be separated by extraction before the precipitation step. In acidic solution, iodine can easily be reduced to iodide by $NaHSO_3$ and then oxidized to I_2 by $NaNO_2$, while chlorine is only reduced to chloride. I_2 is then separated by extraction with CCl_4.[32] The use of two repeat extractions can yield a decontamination factor for iodine of $>10^4$, while the recovery of both chlorine and iodine is $>98\%$.

If measurements of radioactive iodine are not required, iodine can be removed as AgI after the precipitation step. Addition of NH_3 dissolves AgCl but not AgI, so the iodine can be removed by filtration or centrifugation.

The presence of sulfite is troublesome. Sulfite arises in two ways: from the reduction of H_2SO_4 during the digestion process, and as $NaHSO_3$ added to convert iodine to iodide and chlorine to chloride before AgCl precipitation. When sulfite is present, adding $AgNO_3$ will precipitate Ag_2SO_4, Ag_2SO_3, and probably also Ag_2S, as well as AgCl. This consumes a large amount of Ag^+, seriously interferes with the separation of chlorine, and reduces the recovery of Cl—although SO_4^{2-} and SO_3^{2-} can be removed afterward by adding NH_3.

The sulfite problem was solved by the addition of concentrated HNO_3, followed by dilution with water, before the addition of $AgNO_3$. The concentrated HNO_3 oxidizes H_2SO_3 to H_2SO_4, and SO_4^{2-} in dilute solution does not precipitate Ag_2SO_4 when $AgNO_3$

(32) Hou, X. L.; Dahlgaard, H.; Rietz, B.; Jacobsen, U.; Nielsen, S. P.; Aarkrog, A. *Anal. Chem.* **1999**, *71* (14), 2745−2750.

is added. A small amount of Ag_2SO_4/Ag_2SO_3 in the AgCl precipitate can be removed by centrifuging after dissolving AgCl with NH_3. To improve the separation of Cl from the matrix solution, Cl^- in the NH_3 solution can be precipitated again by acidification with HNO_3. The decontamination factors for the main interfering elements and radionuclides are $>10^3$ in this step (Table 3).

Purification of Cl by Anion-Exchange Chromatography. Once the chlorine has been separated by AgCl precipitation, most of the interfering elements and radionuclides can be removed (Table 3). However, the concentration of ^{36}Cl in the sample is normally much lower than that of other radionuclides, such as ^{152}Eu, ^{60}Co, ^3H, ^{14}C, and ^{55}Fe. The measured ratios of $^3H/^{36}Cl$, $^{14}C/^{36}Cl$, and $^{152}Eu/^{36}Cl$ are 10^3-10^5 for graphite and 10^2-10^5 for heavy concrete.[8,10,11,29,30] The measured ratios of $^{63}Ni/^{36}Cl$ and $^{55}Fe/^{36}Cl$ in stainless steel are 1.5×10^5 and 1.4×10^7, respectively. For many waste samples, therefore, further purification to separate Cl from other interfering radionuclides is necessary.

To determine ^{36}Cl using LSC, the separated ^{36}Cl must be mixed with a scintillation cocktail. Precipitated AgCl should be dissolved before mixing with the cocktail to avoid serious quenching by dispersed AgCl particles. Concentrated NH_3 has been widely used to dissolve AgCl,[13,15,18] but this is only suitable for samples containing less than 50 mg of chlorine. Samples derived from graphite, in which $HClO_4$ was used in the dissolution process, contain more than 350 mg of Cl/0.2 g of original graphite and need more than 10 mL of 25% NH_3 to dissolve the AgCl completely. This will significantly dilute the LSC sample and so raise the detection limit of ^{36}Cl.

This problem can be solved by separating Cl^- from Ag^+. This can be done by reducing Ag^+ to Ag and removing Ag as a precipitate. In this case, AgCl is first dissolved in NH_3 solution, after which an excess of hydrazine sulfate[12] or hydroxylamine

sulfate is added to reduce Ag^+ to Ag. Of the two, hydroxylamine sulfate is preferred, because the reaction of hydrazine sulfate with Ag^+ is very slow and needs to be carried out with heating. However, neither hydroxylamine sulfate nor hydrazine sulfate removes other elements apart from Ag. The excess hydroxylamine sulfate also raises the salt content of the Cl solution, increasing the quench in the LSC measurement, and so raising the detection limit of ^{36}Cl.

Anion-exchange chromatography is a better way to separate Cl^- from Ag^+ and other interfering species. Figure 3 shows the separation of Cl^- from Ag^+ for different concentrations of Cl and eluent. Ag^+ in ammonium solution is not adsorbed onto the anion-exchange column, so it can be completely separated from the chlorine. Meanwhile, other metals such as Fe, Co, Ni, Eu, Sr, Cs, and Ba, and tritium, behave similarly to Ag^+ and so are also separated from the Cl.

Elution of Cl^- with too low a concentration of NH_4NO_3 widens the Cl^- peak: the volume of Cl^- eluate when using 0.1 mol/L NH_4NO_3−0.6 mol/L NH_4OH (110−120 mL) as the eluent is twice that when using 0.2 mol/L NH_4NO_3−0.6 mol/L NH_4OH (55−60 mL). The eluent used in this work was therefore 0.2 mol/L NH_4NO_3−0.6 mol/L NH_4OH. The shape of the Cl^- elution peak of for high Cl loading is slightly wider than that for low Cl loading, but the difference is not significant. However, if the Cl load on the column is too high, Cl^- may break through. For an AG1 × 4 column (i.d. 1.0 × 15 cm, NO_3^- form), the maximum Cl^- load before breakthrough was found to be ∼175 mg (Figure S-2, Supporting Information).

Anion-exchange chromatography can also be used to further remove iodine from Cl. Since the affinity of iodide for the ion-exchange resin is much stronger than that of chloride, elution of iodide needs a higher concentration of nitrate (>1.5 mol/L).[32] In this way, we obtained good separation of chloride from iodide ($5.4 × 10^3$) (Table 3).

By separating Cl using AgCl precipitation and further purification by anion-exchange chromatography, decontamination factors of greater than 10^6 were obtained for the interfering radionuclides and elements investigated (Table 3). The γ spectrum of a separated ^{36}Cl sample shows that no γ emitter radionuclides are present, in contrast to an untreated sample with its γ-emitting tracers (Figure S-3, Supporting Information).

Measurement of ^{36}Cl by LSC. After final purification by anion-exchange chromatography, the ^{36}Cl was measured using LSC. Due to the high energy of β particles from ^{36}Cl (708.6 keV) it gives counting efficiencies of 96−99%. The counting efficiency is almost constant for values of the quenching index SQP(E) above 780 (Figure S-1), as well as for different amounts of chlorine as NH_4Cl (Figure S-4, Supporting Information). However, the counting efficiency of ^{36}Cl does vary significantly with chlorine content if the chlorine exists as NaCl or AgCl in NH_3 solution (Figure S-4).

A maximum of 75 mg of Cl in AgCl form or 300 mg of Cl in NaCl form can be mixed with scintillation cocktail (Ultima gold LLT) in a 20-mL vial to obtain a clear solution for LSC measurement with a counting efficiency above 60%. For Cl in NH_4Cl form, as much as 375 mg of Cl can be mixed with the cocktail to obtain a clear solution and without decreasing the counting efficiency (98%). In this work, NH_4NO_3−NH_4OH solution was used as the eluent, so the chlorine in the LSC sample existed as NH_4Cl.

Interference and Analytical Quality Control. The method presented here has been successfully used to separate ^{36}Cl from interfering radionuclides (Table 3, Figure S-3), and for the ^{36}Cl analysis in various materials found in nuclear waste.

The analytical accuracy of the method was verified by spiking samples with a $Na^{36}Cl$ standard. This was necessary since no standard reference materials are available in matrixes similar to those of the samples to be analyzed. In the case of the spiked samples, the measured ^{36}Cl activity concentrations agreed well with the amounts of ^{36}Cl added.

Chemical Yield of ^{36}Cl. The chemical yield of ^{36}Cl was determined by using ICPMS to measure the stable Cl added as a carrier and yield tracer. A 50-mg aliquot of stable chlorine was added to the sample as a carrier. The concentration of Cl in concrete was measured as 48.4 ± 4.1 ppm; the reported concentrations of Cl in graphite, aluminum, and lead samples are below 10 mg/kg, and Parry et al.[26] reported less than 2 mg/kg Cl in several types of steel. Since less than 5 g of sample was used in this work, the contribution of Cl from the sample (<0.1%) can therefore be ignored. The measured chemical yield is 80−90% for concrete, 90−99% for lead, and 75−85% for steel and aluminum. The slightly lower chemical yield for steel may result from the loss of some Cl in the AgCl precipitation step, due to interference by the high concentrations of H_2SO_4/H_2SO_3 used to decompose the steel samples.

Chlorine has many different chemical forms, including Cl^-, Cl_2, ClO^-, ClO_2^-, ClO_3^-, and ClO_4^-. Of these, Cl^- is the most stable, while ClO_3^- may also exist in nature. Both NaCl and $NaClO_3$ were added to the sample as carriers, and they showed the same chemical yield (Table 2).

For graphite, the $HClO_4$ used in the decomposition solution will also act as a chlorine carrier. A high chemical yield (85−100%) was obtained for the graphite samples.

Detection Limit. The detection limit of the method is limited mainly by the LSC blank counts, variation of the blank counts, chemical yield, counting efficiency, and amount of sample. This work used an ultralow-level liquid scintillation counter, the Quantulus 1220. The counting ranges were channels 100−820, and the blank counts were 5.2 ± 0.30 counts/min, measured for 60 min. The average counting efficiency under working conditions was measured as 97.5%. The detection limit is given by

$$L_d = 4.65(SD_b/n^{1/2})/\eta$$

where SD_b is the standard deviation of the blank counts (counts/min), n is the number of blank samples (three, in this case), and η is the counting efficiency.

Using these figures, L_d can be calculated to be 14 mBq. This work used samples weighing 0.2 g for graphite, 1.0 g for steel, aluminum, and concrete, and 5 g for lead; the calculated detection limits for ^{36}Cl in these materials are therefore 69, 14, and 2.8 mBq/g, respectively. It is clear that, for ordinary nuclear waste samples, this method is sensitive enough for the determination of ^{36}Cl.

SUPPORTING INFORMATION AVAILABLE

Additional information as noted in the text. This material is available free of charge via the Internet at http://pubs.acs.org.