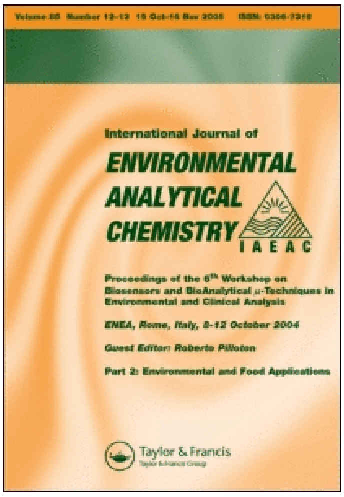

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ACCURATE DETERMINATION OF ^{113m}Cd IN ENVIRONMENTAL SAMPLES*

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^{113m}Cd($t_{1/2}$14.6y, β^-) entered the environment during testing of thermonuclear weapons in the atmosphere. It has been detected in water and sediments of the Laurentian Great Lakes, and in marine biota both near to and remote from the test sites. The isotope has potential as a biogeochemical tracer for natural Cd, provided it can be determined accurately. Because ^{113m}Cd decays by emission of low energy β^- particles, and because its concentration in environmental samples is extremely low, earlier reports of ^{113m}Cd detection were based on chemical inference alone. We have now demonstrated conclusively that ^{113m}Cd may be determined accurately at levels on the order of 100 μBq l^{-1} in water and 1 mBq g^{-1} in sediments. Our evidence consists of reverse tracer analysis in two different systems, and modified Feather analysis using graded Al absorbers.

Dithiolate complexes of Cd were partitioned between $CHCl_3$ and water, and between pH 6.3 buffer and ion exchange resin. In both systems, phase distribution of the radio-cadmium was statistically indistinguishable from that of added stable Cd tracer. In Al absorbers, the range-log countrate curve for suspected ^{113m}Cd isolates yielded E_{max} for the β^- particles of 0.66 ($\pm$0.07) MeV, compared to the accepted value of 0.59 MeV.

KEY WORDS: Cadmium, biogeochemical tracer, water sediments.

INTRODUCTION

The occurrence of a long-lived radioisotope of cadmium in the environment was first recognized by Salter.[1] ^{113m}Cd ($t_{1/2}=14.6y$, 99.9% β^-, 0.01% γ) entered the global environment as a result of the testing of thermonuclear devices in the atmosphere: the cadmium-clad STARFISH device produced 0.13 MCi by a ^{112}Cd(n,γ) reaction, while other tests produced a comparable amount due to thermonuclear fission. ^{113m}Cd was recognized as an important, although unexpected result of high altitude tracer tests.[2,3] Oddly its utility in biogeochemical studies has gone largely unexplored. Noshkin reported detecting it in shark's liver from Bikini, and in the liver of mullet from the eastern coast of North America.[4]

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Palagyi and Larsen determined ^{113m}Cd in 55 l samples from Lake Michigan, albeit very near the method's limit of detection.[5] Recently, we explored its occurrence in Lake Michigan in more detail.[6]

The major obstacle to using long-lived weak β^--emitting nuclides as environmental tracers is specificity. Environmental samples typically contain many β^- emitters, and usually only the gross β^- activity can be measured in isolates. For an isotope with a long half-life and low activity, neither E_{max} for the β^- particles nor the half-life can be determined. Thus the specificity with which one can measure such a nuclide depends on the degree to which it can be decontaminated, i.e., freed of all other β^- emitters. In such circumstances, accuracy rests wholly on negative inference, with all the attendant risks.

We now report confirmation of ^{113m}Cd in isolates from water, sediment, and soil. Our evidence consists of a determination of E_{max} for the observed β^- activity using range-energy relationships in graded aluminum absorbers, plus reverse tracer analysis in two different partitioning systems.

EXPERIMENTAL

Isolation, Soils and Sediments

Lake sediment and soil were collected with standard sampling gear, homogenized, dried in air at 105°, and ashed at 480° for 12 h. Subsamples of 10 g were amended with 1.0 mg of stable Cd carrier, leached with five successive portions of conc. HNO_3-HCL (9:1 v/v), and digested at reflux for 4 h. The supernatant was collected following centrifugation at 1000 × g, combined with two 50 ml water washes, filtered through Whatman No. 1 paper, evaporated to dryness, and then taken up in 0.3 l of 1 M HCl.

Lake Water

Lake water (typically 1000 l) was collected through 1.5" i.d. Tygon tubing using a high capacity deck pump. The sample was acidified to $pH < 2$ with conc. HNO_3, and Cd, 1.0 mg, and Fe, 1.0 g, were added as carriers. After stirring vigorously for 1 h, the pH was brought to 9 with 50% w/w aqueous NaOH. The resulting suspension was stirred for 1 h, then allowed to stand for 1–12 h. The supernatant liquid was pumped without disturbing the settled solids through 293 mm dia., 0.45 μm cellulose acetate membrance filters using a seven-stage high volume filtrator (One-Sevener, Nuclepore Corp.). Insoluble material in the final 50 l was then resuspended in the remaining liquid and collected with frequent filter changes. The laden filters were transferred to a 1 l beaker and dried in air at 105° for 5 h. Conc. HNO_3, 50 ml, was added and the sample was dried and ashed at 380° for about 2 h. The residue was suspended in 0.1 l of 6 M HCl, then filtered through Whatman No. 1 paper. The collected solids were washed twice with 50 ml portions of 6 MHCl. The combined filtrate and wash liquids were diluted to 1 M HCL.

Decontamination

The ^{113m}Cd isolates in 1 M HCl were applied to an anion exchange column (Dowex 1×8, 50 ml bed, 2 ml min^{-1} flow rate.) The column was washed with 10 column volumes of 1 M HCl and then with 10 column volumes of 0.5 M HBr. Cd was eluted with 0.5 l of 7.5 M NH_3(aq.). The ammoniacal eluate was taken to dryness and the residue redissolved in 100 ml of 1 M HCl. Cu, 5 mg, was added, the pH adjusted to 8 with 10 M NaOH, and the Cd and Cu were precipitated by adding 10 ml of 1 M thioacetamide and digesting at 80–90° for 1 h. The precipitate was collected on a 25 mm dia., 0.45 μm cellulose acetate membrane. The dried filter was centered on a 38.1 mm stainless steel planchet which had been previously covered with double-sided adhesive tape. The annulus of adhesive remaining exposed was used to affix a cover of 6.3 μm Chemplex film.

Absorber Range Determination

A ^{90}Sr sample was freed of ^{90}Y by collecting the daughter on freshly precipitated $Fe(OH)_3$. Sr was collected as the carbonate by precipitating with $NaHCO_3$ in the presence of a Ca carrier. The β^- activity in this ^{90}Sr standard and the isolates of ^{113m}Cd was counted using a Tennelec Model LB 4000 gas proportional counter. Graded high purity Al absorbers were interposed successively between source and detector by placing them directly on top of the samples.

Reverse Tracer Analysis. Procedure A

Individual filter membranes bearing ^{113m}Cd isolates were removed from the planchets on which they had been mounted and triturated in isopropanol. The resulting slurry was taken to dryness, then dissolved in 10 ml of 6 M HCl and diluted to 150 ml. Sufficient Cd, as $CdCl_2$ in 6 M HCl, was added to bring the total Cd to 5 mg. After adjusting the pH to 12 with 10 M NaOH, 250 ml of 1% aq. ammonium pyrrolidine carbodithioate was added along with 25 ml of redistilled chloroform. The two layers were vigorously emulsified, then separated in a separatory funnel. The organic phase was covered with 50 ml of 6 M HCl and heated gently until the chloroform had evaporated. The resulting solution, and the original aqueous phase, were taken to near dryness, then diluted to 150 ml with deionized water. Cd was precipitated as the sulfide by the method described earlier. β^- activity was assayed in these samples by the usual counting procedure, while stable Cd was determined by X-ray energy spectrometry.

Reverse Tracer Analysis. Procedure B

The capacity of Amberlite XAD-4 resin for the bis(2-hydroxyethyl)dithiocarbamate complex of Cd^{2+} was determined as follows. Sodium bis(2-hydroxyethyl)dithiocarbamate, 2.5 g, was added to each of three 200 ml aqueous solutions containing

2.75 mg of Cd. Each solution was treated with 2 ml of saturated ammonium acetate, and adjusted to pH 6.3 by the addition of dilute HCl or NaOH. A small amount of XAD-4 resin was added to each solution and stirred for 30 min. The resin was collected by vacuum filtration, then stripped with 25 ml of 10% ethanolic HNO_3. These solutions, along with the filtrates, were analyzed for Cd by atomic absorption spectroscopy.

Two composites of ^{113m}Cd isolates, one from lake sediment (I) and the other from lake water (II), were treated with stable Cd to bring the total concentrations to 5 and 6.5 mg, respectively, then digested in conc. HNO_3 until clear. Both samples were taken to dryness. The residue from I was dissolved in 1 M HCl and applied to a Dowex 1 × 8 anion exchange column. Following removal of Cu with 1 M HCl, Cd was eluted with 0.3 l of 1 M HNO_3. Sample II did not contain Cu from previous handling and was taken up directly in 0.3 l of 1 M HNO_3.

Both samples were brought to pH 6.3, buffered with 10 ml of saturated ammonium acetate, and treated with 2.5 g of sodium bis(2-hydroxyethyl)dithiocarbamate. Samples I and II received 0.9488 g and 1.1301 g of XAD-4 resin, respectively. The resulting suspensions were stirred for 30 minutes. The supernatant was separated by vacuum filtration and reserved. The resin was stripped with 25 ml of 1 M ethanolic HNO_3 to remove absorbed Cd. Both the supernatant and the stripping solution were taken to dryness, redissolved in 0.15 l deionized water, and brought to pH 8. The absorbed and unabsorbed fractions from both samples were precipitated as the sulfides in the manner described previously, and assayed for Cd by X-ray energy spectrometry.

Sampling Locations and Characteristics

Water samples were collected from Lake Michigan at two locations: approximately 15 miles offshore from Grand Haven, Michigan (43°00'N by 77°33'W), and from the Grand Haven municipal water supply. Sediments were sampled at the offshore location. Soil cores ($864 cm^2$ to a depth of 5 cm) were collected in southwest suburban Chicago at undisturbed sites routinely used by Argonne National Laboratory personnel for fallout nuclide determinations. The mean ^{113m}Cd activities (shown with the 95% confidence interval) were $350 \pm 150\,\mu Bq\,l^{-1}$ and $10.0 \pm 5.6\,mBq\,g^{-1}$ for the water and sediment samples, respectively. In the soil cores, the mean $^{113m}Cd/^{137}Cs$ activity ratio was 0.023 ($s = 0.012$), based on Golchert's ^{137}Cs data.[7]

X-ray Energy Spectrometry

Stable Cd was determined in the sulfide precipitates by X-ray energy spectrometry (XES).[11] The spectrometer consisted of a 75 kV constant potential high voltage generator (General Electric, Model XRD-6), a W-anode tube (Amperex), and a vacuum sample changer and detector-preamplifier (Canberra, Model 0810). Pulses were processed with a Canberra 4020P amplifier, digitized with a Canberra 8100 multichannel analyzer, and stored on magnetic media.

The XES device was operated in the 2° source mode. Radiation from the X-ray tube operated at 55 kV excited a Ba 2° source, which in turn produced Cd K-X-rays in the samples. A $100\,\mu m$ Al disk was used to limit the flux of low energy photons to the detector. Under these conditions, the 3σ detection limit for Cd was below $1\,\mu g$ for a $10^3 s$ counting time. Standards for calibrating the response of the instrument were prepared by coprecipitating stable Cd and Cu as the sulfides in the presence of ^{109}Cd as a tracer. Recovery efficiencies were calculated from the ratios of the integrated ^{109}Cd photopeaks in the spiked standard to the photopeak integrals from the same amounts of ^{109}Cd applied directly to blank filters. The resulting set of absolute standards (100–2000 μg Cd) gave a linear calibration curve with a correlation coefficient of 0.99 and a negligible intercept.

γ-Ray Counting

γ-Rays were counted with a NaI(TI) scintillation detector (EG & G Ortec Inc.). The photomultiplier lead was fed through one wall of a $1\,m^3$ lead-shielded vault to the multichannel analyzer. Background countrates near the region of interest were integrated hourly, in duplicate, and background corrections were made using three sets of these values.

DISCUSSION OF RESULTS

Palagyi and Larsen's procedure for scavenging ^{113m}Cd from lakewater involves precipitating $10\,mg\,l^{-1}$ of Fe as $Fe(OH)_3$ at pH 7 from 50 l samples.[5] In order to increase the reliability and precision of the determinations, we modified their procedure for use with $1\,m^3$ samples. To avoid handling excessive quantities of $Fe(OH)_3$, it was necessary to increase the Cd/Fe mole ratio (Γ) from their value of ca. 9×10^{-6} to 5×10^{-4}. This led initially to low recoveries, but studies with ^{109}Cd tracer showed that the pH for optimum recovery shifted to higher values as Γ increased. At pH 9 the efficient absorption of Cd on the $Fe(OH)_3$ carrier was restored. For the optimized procedure, scavenging from lake water had a mean efficiency of $80 \pm 12\%$.

The principal difference between our decontamination scheme and that of Palagyi and Larsen[5] is the addition of a step in which Zn is eluted from the ion exchange column with 0.5 M HBr. This step eliminates the possibility of interference from ^{65}Zn, which is occasionally released in measurable amounts in liquid wastes from nuclear electric power reactors. In dilute HBr, the distribution coefficient for Zn on the anion exchange resin is <6, while that for Cd remains above 10^6 up to 9 M HBr. Studies with ^{65}Zn and ^{109}Cd tracers confirmed that more than 99% of added Zn is removed with 10 column volumes of 0.5 M Br, while Cd is quantitatively retained.

Two other isotopes are potential interferences: ^{227}Ac and ^{210}Pb. Actinium is not

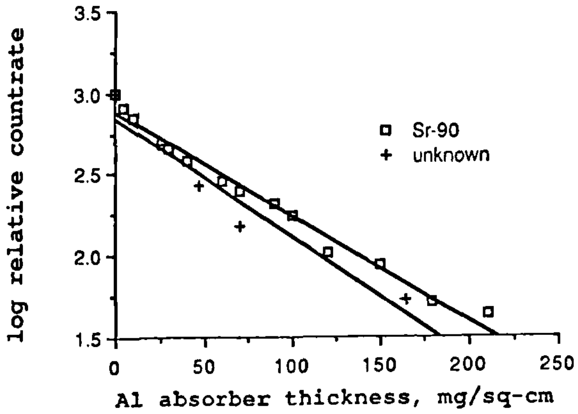

Figure 1 Comparison of relative countrate vs. absorber thickness for authentic ^{90}Sr and suspected ^{113m}Cd.

absorbed by anion exchangers, and its low E_{max}(0.043 MeV) allows range-energy discrimination, *vide infra*. Lead is effectively removed from the resin along with Fe using dilute HCl. However, relatively high ^{210}Pb activities are found in Lake Michigan superficial sediments (250–850 mBq g^{-1}.) The following evidence confirms that it is in fact eliminated in the decontamination scheme.

^{210}Pb decays by β^- emission to ^{210}Bi($t_{1/2}$=5 d, 99% β^-, 1% α). Assuming secular equilibrium, either ^{210}Bi or ^{210}Po can be used to assess ^{210}Pb. Isolates from our decontamination scheme exhibited no statistically significant α activity from ^{210}Po. Furthermore, the fast growth of ^{210}Bi in samples containing ^{210}Pb would manifest itself by an increase in β^- activity. No such increase was observable.

^{90}Sr($t_{1/2}$=27.7*y*, 100% β^-) is conservative in Lake Michigan, and its present concentration[8] is about 25 mBq l^{-1}. Thus in order to reduce the interference from it to a value less than 10% of the expected ^{113m}Cd activity, the degree of decontamination must be at least 10^3. Fortunately, Sr, along with Y, Sc, Ni(II), Th(IV), and the alkali and alkaline earth metals, are not absorbed by Dowex 1 × 8 from 1 M HCl.[10]

Aluminum absorbers of varying thickness were used to determine the range, and hence the maximum energy (E_{max}), of the β^- particles from the composited ^{113m}Cd isolates. Figure 1 displays the results, along with similar data from a freshly prepared ^{90}Sr source, normalized to equal initial countrates. The lines represent least-squares linear regressions. E_{max} for ^{90}Sr, 0.55 MeV, is very nearly the same as for ^{113m}Cd, 0.59 MeV.[9] Thus the two absorption plots should nearly coincide, as they do within the experimental uncertainty. This result establishes that the principal β^- emitter in the isolates has an E_{max} qualitatively indistinguishable from authentic ^{113m}Cd.

To substantiate this finding, we used a procedure known as modified Feather analysis to calculate E_{max} from the absorption data. The maximum range of the β^- particles from a given source cannot be measured directly by incrementing

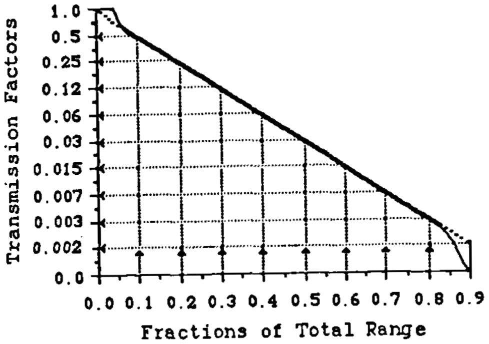

Figure 2 Transmission factor, t_f, as a function of range of particles (expressed as a fraction of total range).

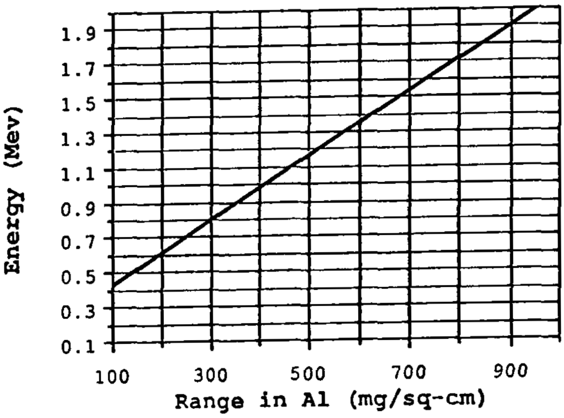

Figure 3 $E_{\max}$ for particles vs. total range in Al absorbers.

absorber thickness until the countrate becomes nil, due to the statistical uncertainty in the countrates with thick absorbers. Modified Feather analysis[13] avoids this difficulty by using only data from the initial portion of the absorption curve. This procedure is based on the concept that, to a good first approximation, the total corrected activity can be assigned a transmission factor, t_f, of unity at absorber thickness, z, equal zero, and t_f of 0.5, 0.25, and 0.125 at absorber thicknesses equal to $0.1z_\omega$, $0.2z_\omega$, and $0.3z_\omega$, respectively, where z_ω = maximum range, as shown in Figure 2. In other words, t_f decreases by a factor of 2 for each increase in absorber thickness corresponding to $0.1z_\omega$.

The absorption curve in Figure 1 is described by log countrate = -0.01 (range, mg cm^{-2}) + 2.94 ($r = -0.99$). This relationship was used to calculate z_1 for countrate$_1$, and z_2 for countrate$_2$ = 0.5(countrate$_1$). Then $z_\omega = 10(z_2 - z_1) =$ 225 mg cm^{-2}. From this value of z_ω, $E_{\max}$ was evaluated from the effective range-energy curve for β^- particles in Al shown in Figure 3, giving a value of 0.66 (± 0.07) MeV, compared to the accepted value of 0.59 MeV.[9]

Table 1 Reverse tracer analysis.[a, b]

Sample	*Procedure A*	
	Organic phase	*Aqueous phase*
1	1.1±0.1	0.9±0.1
2	0.8±0.1	1.2±0.1
3	0.7±0.1	1.2±0.1
4	1.5±0.2	0.8±0.1
5	1.8±0.2	0.6±0.1
	Procedure B	
	Aqueous phase	*Sorbed phase*
6	1.0±0.1	1.1±0.3
7	1.1±0.1	0.9±0.1
	Mean ± 1*s* = 1.1 ± 0.5	

[a] The values are normalized specific activities in each phase.

[b] The uncertainties shown are those due to counting statistics alone.

The radiometric analysis establishes that the isolates have the same emissions characteristics as ^{113m}Cd. However, the possibility exists that these characteristics are due to another radionuclide, or mixture of radionuclides of some other element(s). While we have no candidate isotopes to suggest, given the chemistry of the isolation and decontamination scheme,[4,5] we undertook to establish more rigorously the radiochemical identity of the emitting species by using reverse tracer analysis (RTA). RTA is a stringent test of radiochemical purity that uses phase partitioning based on chemistry independent of the decontamination scheme. It involves the addition of a known amount of the corresponding stable isotope to the sample, followed by a partition of the element between two phases. If the emitting isotope is radiochemically pure, the radioactivity present should partition identically to the stable isotope. Interfering emitters presumably would partition differently, signalling their presence by a discrepancy in the partitioning of the gross β^- activity and the added stable tracer.

We carried out the RTA procedure using two schemes. In Procedure A, the complex of Cd^{2+} with pyrrolidine carbodithioate was allowed to partition between $CHCl_3$ and a pH 12 aqueous solution. Procedure B involved the equilibrium absorption onto Amberlite XAD-4 resin from aqueous solution at pH 6.3 of the bis(2-hydroxyethyl)carbodithioate complex of Cd^{2+}. Replicates consisted of isolates from water and sediment samples collected at different times and places. The partitioning of the stable isotope was evaluated by X-ray energy spectrometry.[11] The results of these experiments are shown in Table 1.

The samples had different specific activities, and the recovery efficiency showed some variability. Therefore the data are presented as normalized specific activities, i.e., the fraction of the total β^- activity found in a given phase, divided by the fraction of the total stable Cd in that phase. This dimensionless quantity permits direct comparison of the various samples. Equipartitioning of the radioactivity and the stable tracer is indicated by a value of unity for the normalized specific activities in both phases. Clearly not all the values are unity, and the mean is 1.1 ($s = 0.5$). However, the value of t^* calculated for these data was 0.7. This indicates there is a 55% probability of locating the true mean within ± 1s of 1.1.[12] This test of significance was made with a 10% difference between the observed and expected mean values, while a 28% difference would have been required to reject the hypothesis that the stable and radiocadmium partition identically. RTA analysis in two systems thus failed to uncover the existence of β^- emitters in the isolates that were chemically distinguishable from Cd. Within the experimental uncertainty, the identity of ^{113m}Cd is confirmed.

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