

A method for the detection of Tc in seaweed samples coupling the use of Re as a chemical tracer and ID-ICP-MS.

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Abstract.

The analysis of artificial radionuclide ⁹⁹Tc in environmental samples requires of a chemical separation due to its low concentration, and therefore the use of a chemical yield tracer is peremptory. From the practical viewpoint, Re could be used for these purposes, due to the chemical similarities between Re and Tc. Thus, the use of a radioactive tracer for Tc recovery calculation could be avoidable. However, results from the more recent intercomparison exercise shows that the use of Re as a chemical yield tracer appears to underestimate the Tc concentration relative to the result obtained with isotopes of Tc. In this work, we show the methodology used for designing a simple separation method for the measurement of ⁹⁹Tc in environmental samples. Tc recovery is estimated throughout the Re recovery calculation by the ID-ICP-MS technique. For chemical separation, a chromatographic resin has been used. Interfering elements are removed using a resin washing step carefully designed to avoid any element fractionation between Re and Tc, being this step of major importance to assure the equivalence of the chemical recoveries for both elements. Such an agreement was tested using 5 replicates of five seaweed samples. The average recoveries for ^{95m}Tc and Re were 93±6% and 95±7%, respectively, those were within the uncertainty intervals for each other. The results here explained demonstrated the possibility of applying Re chemical recoveries to calculate the Tc concentrations with the advantage of not introducing systematic errors.

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1. Introduction.

Technetium-99 (2.1×10^5 y of half-life) is a low-energy beta-emitter formed as a fission fragment with a relatively high fission yield ($\sim 6\%$). Controlled radioactive releases from the large nuclear fuel reprocessing plants of La Hague (France) and Sellafield (UK) have been the major sources of this radionuclide in North Atlantic seawater, even in competition with the global fallout source. It will be predominately present in seawater under oxic conditions in the form of TcO_4^- ion, which is extremely stable and it could be carried out far from these sources, following the general circulation of the ocean currents [1]. Indeed, such stable characteristics allow the researchers to use it as a radioactive tracer for the movement of water marine masses and marine currents. Furthermore, several biota species with a high accumulation capacity for this element have been identified [2], such as brown algae, especially those of *Fucus Vesiculosus* specie. This fact suggested their use as a bioindicator for technetium concentrations in seawater [1].

As a fast and very sensitive alternative to radiometric detection, ICP-MS has been proposed for the ^{99}Tc determination in environmental samples. Hence, quadrupole ICP-MS instruments with pneumatic [3-6] or ultrasonic nebulizers [7], Electrothermal Vaporization units (ETV-ICP-MS, [8]), Laser Ablation units (LA-ICP-MS, [9]) and High Resolution ICP-MS [10] have been used for ^{99}Tc detection in a variety of industrial and environmental samples. However, the chemical separation and

purification of Tc from environmental samples is needed. To achieve this, a wide variety of isotopes has been used as yield monitors in the determination of ^{99}Tc in environmental samples. Usually, $^{99\text{m}}\text{Tc}$ [11-12], $^{95\text{m}}\text{Tc}$ [13] and $^{97\text{m}}\text{Tc}$ [14] have been used. These isotopes are generally determined using gamma-ray spectrometry. Beals [15] proposed the Isotope Dilution technique coupled with ICP-MS (ID-ICP-MS) using ^{97}Tc as a yield tracer. The main advantage of the ID technique is in overcoming the problems associated with instrumental drift and matrix effects. Furthermore, the ID-ICP-MS technique relies purely in isotopic ratios; therefore the problem of an incomplete extraction is negated.

It is well known that Re and Tc chemistries are similar: their analogous compounds are virtually identical from a structural standpoint. Therefore, Re has been proposed as a tracer for ^{99}Tc radiochemical recovery calculation from environmental samples, both for radiometric [16] and non-radiometric [17] counting methods. The first of these methods [16] follows a chemical separation based on coupling 1) the use of an anion exchange resin to concentrate Tc (and Re), 2) a precipitation step of Tc and Re as sulfides, from a NaClO_4 solution, and 3) a precipitation step of Re and Tc as tetraphenyl arsonium salts. Chemical yield is determined by gravimetric analysis of the rhenium salt. The second method [17] is applied after a chemical separation scheme based on the use of a TEVA·Spec chromatographic resin, although unfortunately analytical details are still to be published.

Nowadays, Re is used routinely for this purpose with few problems reported. This approach avoids the use of radioactive isotopes, especially at the place where these

radioisotopes are strictly forbidden (e.g., on a ship for seawater sampling). Furthermore, using Re avoids the analytical implications of the use of another isotope of Tc: common nuclear reactions for ^{97}Tc and $^{95\text{m}}\text{Tc}$ generation produce also ^{99}Tc , which cannot be removed from the yield tracer solution [16]. An alternative reaction that produces $^{95\text{m}}\text{Tc}$ free of ^{99}Tc has been described elsewhere [13], but this option is only available to those laboratories provided with a cyclotron.

However, the results from a recent intercomparison exercise for ^{99}Tc in seaweed samples shown that those laboratories who used Re as a chemical yield tracer, systematically underestimated the Tc concentrations by more than 20% on average [18]. This fact could be due possibly to an overestimation of the recoveries for Tc.

The main difference between Re and Tc is in their respective oxidation potentials; the reduction of Re is more difficult than that of Tc [19]. Thus, slightly different coprecipitation profiles for ReO_4^- and TcO_4^- ions with TPAC, and different elution profiles from an anion exchange resin have been shown [16]. More recently, the differences in the capacity factors for Tc and Re using the same chromatographic resin have been shown [20]. Those small chemical differences should be considered in detail if a new method that uses Re as a chemical yield tracer for Tc is to be designed.

In this work, a new method that uses Re ID-ICP-MS detection for Tc chemical yield calculation is proposed. In this way, data for Tc solution concentration and chemical yield could be achieved using the same analytical running with an only instrument. This methodology offers the following advantages: 1) Radiological concerns due to

radioactive tracers handling are avoided 2) ID-ICP-MS improves the precision of the Re chemical yield calculation 3) The method takes into account explicitly the small differences between the Re and Tc chemical behavior. Hence, the problem of the Tc concentration underestimation could be avoided. 4) The ID-ICP-MS technique allows the determination of both Tc concentration and chemical yield simultaneously; therefore additional techniques (such as gamma spectrometry for Tc isotopes recovery calculation or gravimetric analysis for Re recovery calculation) are unnecessary.

This paper focuses on the methodological aspects of the separation scheme proposed, and on its justification. The equivalence for Re and Tc recoveries is tested using some seaweed samples. There are no suitable reference materials with ^{99}Tc certified concentrations. Therefore, several seaweed samples from the North Atlantic Ocean were subjected to this purpose.

2. Experimental

2.1. Samples and chemicals

Five samples of brown algae (*Fucus* sp.) were taken on the coast of Utsira, southwest of Norway, in the year 2000 on a monthly basis. Dates of collection are provided on Table 1. Samples were periodically taken in the framework of an evaluation program of environmental radioactivity in the Nordic waters [21]. Five replicates of every sample were analyzed for comparing the results obtained in this work for Re and Tc chemical yields.

After the collection, seaweed samples were dried up, and the sediment particles were removed by shaking. Using a mechanical sample homogenizer, the samples were homogenized. Then, the samples were transferred to cylindrical PEEK beakers, and then they were sealed for transportation.

Nitric acid used was ultrapure-analytical grade (Tama AA-100; Tama Chemicals Co. Ltd, Kanagawa, Japan). Deionized water ($>18\text{ M}\Omega$) was obtained from a Milli-Q water system (Nihon Millipore K.K; Tokyo, Japan). Prepacked columns of Tc-selective chromatographic resin (TEVA, Eichrom Industries, Inc; Sowa Trading Company, Inc., Tokyo, Japan) were used for separation of Tc and Re. The high selectivity of this resin for ReO_4^- and TcO_4^- has already been reported [20,22].

A radioactive tracer, $^{95\text{m}}\text{Tc}$ (half-life: 61 d, chemical form: TcO_4^-), was used for ^{99}Tc and enriched ^{185}Re (chemical form: ReO_4^-) was used for Re. The carrier-free $^{95\text{m}}\text{Tc}$ was separated from a Nb foil irradiated with alpha particles [13]. The ^{185}Re isotope enriched solution was produced dissolving a suitable amount of the solid supplied by the Oak Ridge National Laboratory (TN, USA) ($96.74 \pm 0.01\%$ isotopic abundance of ^{185}Re) to 6M HNO_3 . Using both yield tracers, it would be possible to compare their respective chemical yields for each sample replicate using isotope dilution technique, as natural abundances are 37.40% (^{185}Re) and 62.60% (^{187}Re).

2.2. Separation Method

The samples were oven dried at $65\text{ }^\circ\text{C}$. Then, 0.5-g amount of each sample was transferred to a porcelain crucible and spiked with 25 Bq of $^{95\text{m}}\text{Tc}$ (approximately 30 fg)

and 35 ng of the ^{185}Re -enriched solution, respectively. Then the samples were subsequently taken to an electrical oven.

Three different sample pretreatment methods were compared, in order to optimize this step: A) the sample was heated at 450°C for 30 minutes, then, the residue was dissolved using 5 ml of 4M HNO_3 at 120°C for 3 h; B) heating the sample at 450°C for 90 min, the residues were then dissolved using leaching with 5 ml of 4M HNO_3 at 120°C for 3 h; C) heating the sample at 450°C for 90 min., the residues were then dissolved using leaching with 5 ml of 8M HNO_3 at 120°C for 3 h. For all the methods, the samples were heated under reflux, to avoid any loss of Tc and Re. This heating step under acidic condition assures the oxidation of the Tc transferred to the liquid phase [23].

After the incineration, the sample was cooled down to room temperature and it was filtered by gravity using filter paper (Toyo 5-C; Toyo Roshi Kaisha, Ltd. Tokyo, Japan). The filter was washed with deionized water and the wash and the filtrate were transferred into a 250 ml polypropylene bottle. This solution was diluted down to 200 ml with deionized water.

Then, the TEVA resin was used to concentrate the Tc and Re [24]. This extraction chromatographic resin is an aliphatic quaternary amine. Capacity factors as high as 6×10^3 have been reported for Re. [20]. It has been used for Tc analysis because its high selectivity for Tc from environmental analysis [12,15,22,25] when Tc is loaded onto the resin as pertechnetate ion in a diluted nitric acid solution. Prepacked minicolumns (4.2

cm length, 0.8 mm diameter, mesh sieve 100-150 μm) of this amine, which is sorbed on Amberchrom CG71, were used in these experiments.

Following previous experiments developed at NIRS [26-27], the minicolumn was preconditioned with 5 ml of 8M HNO_3 and 10 ml of 0.1M HNO_3 , using free flow. A flow rate of 1.4 ml min^{-1} was used to load the sample solution onto the resin. A resin washing step is necessary in order to remove the interfering elements for ICP-MS analysis (such as W for Re and Mo and Ru for Tc respectively). For ^{99}Tc analysis in soil samples, 2M HNO_3 is used [27]. However, according to those experiences previously mentioned, this nitric acid concentration would remove a great fraction of Re contained onto the resin, but Tc should be retained on it. This fact would cause a fractionation of Re and Tc atoms, which could produce an underestimation of the chemical yield. On the contrary, if 2M HNO_3 were used as stripping solution, Re would be eluted, while Tc atoms would be retained onto the resin. This fact would cause an overestimation of the chemical yield. Therefore, both approaches were avoided.

20 ml of 1M HNO_3 were used for washing the column. Such a process of resin washing is not a novelty; however the nitric acid concentration used is a necessary change in this chemical separation scheme, in order to avoid analyte/tracer fractionation. This washing process removes interfering elements for ICP-MS analysis without affecting the Re and Tc retained fractions in the resin [24, 26].

Both Re and Tc were stripped from the resin using 5 ml of 8M HNO_3 . Previous works [22,24] have shown the high efficiency of this stripping process.

The concentration of nitric acid is not suitable to be aspirated by the ICP-MS instrument; thus, the solution was heated to near dryness on a hot plate. The temperature was always less than 75°C to avoid any Tc and Re loss in the evaporation process. Finally, the solutions were diluted to 15 ml with deionized water. An alternative to this process would be a simple sample dilution to a 0.1M HNO₃ solution. However, this method would increase the analyte's dilution factor, and, thus, this alternative would increase the limit of detection of the technique by a factor greater than 25 respecting that other method here proposed.

2.3. Apparatus.

The gamma rays emitted by the ^{95m}Tc were measured on an Aloka ARC-300 NaI(Tl) scintillation counter (Tokyo, Japan) in order to calculate the Tc chemical yield. The chemical yield for Re was calculated using the isotope dilution method with the ICP-MS (HP-7500, Yokogawa, Japan). Indium was used as internal standard for Mo, Ru and Tc. Operating conditions are provided on Table 2. In order to minimize the error propagation when applying the ID method, the optimum ¹⁸⁵Re/¹⁸⁷Re isotopic ratio was calculated according to the expression (PLEASE, CHECK REFERENCE) $R_{opt} = (R_N \times R_S)^{1/2}$, being $R_{opt} = 4.21$ the optimum isotopic ratio, R_N the natural isotopic ratio and R_S the spike isotopic ratio.

For recovery calculation, the ¹⁸⁵Re/¹⁸⁷Re isotopic ratio determination in the analyzed solutions is required. To do that, the instrumental mass bias was determined off-line. A

linear correction algorithm was used. Typical mass-bias factors throughout this study were in the range of 3% per mass unit.

For Tc, major interferences are those arising from Ru (^{99}Ru , 12.6 %) and Mo ($^{98}\text{Mo}^1\text{H}$, 24% and ^{100}Mo , 9.6%) isotopes present in the analyzed solution. Concerning Re, it is possible to generate isobars by forming hydrides with W isotopes at masses 185 and 187. The developed method was checked for the potential to generate isobars in each measurement. To do that, masses 95 and 98 (Mo), 101 and 102 (Ru) and 182 (W) were analyzed.

3. Results and discussion.

3.1. Mass spectrum.

As explained above, the possibility of forming counting interferences was checked for every analysis. The Mo concentrations in the solutions were always in the range of 0.02-1.10 ng/ml. This range of concentrations does not produce remarkable interferences on ^{99}Tc spectrum [28]. For seaweed samples, the concentration of Ru in the final solution is not high: the responses obtained for Ru isotopes reproduced those obtained for blank solutions. In the case of soil samples, we should pay attention for separation of Ru from the final solution. On the other hand, the concentration of W in every sample was in the range of 0.1-70 pg/ml. Hence, no interference on the mass spectra of Re is expected.

3.2. Recoveries for Technetium and Rhenium.

The Re and Tc chemical yields were checked using three methods of separation, as described above. The results are listed in Table 1. Using the method A, we found that the percent of mass loss after reducing the samples to ashes was lower than 25%. This value did not correspond to biological samples. This means that the organic matter was not completely removed from the samples using this procedure. Therefore, the extraction of Tc from the sample could possibly be incomplete. This would cause the lower chemical recovery shown in Table 1. Using the method B, we found better recoveries, because the organic matter was removed more efficiently after increasing the time devoted to reduce the samples to ashes. Furthermore, the concentration of HNO₃ used in the leaching process was half of that used in method C. However, it seems that there are no systematic differences between the results achieved using the methods B and C. Thus, 4M HNO₃ could be a suitable concentration of nitric acid to extract the Tc retained in the ashes, at least when so small sample masses are analyzed. However, the possibility of applying this method for soil or sediment samples is under consideration. As 8M HNO₃ is commonly used for this kind of samples instead of 4M HNO₃, the method C was used in this work.

The method C was applied to five aliquots of every sample, as described above. The results obtained for both the recoveries of ^{95m}Tc and Re are shown in Table 3. These recoveries are the same, within an uncertainty interval of 1σ. The fourth replicate of the sample 3021 is the only exception. A weighted linear fit was generated, which produced a correlation coefficient of 0.92. The slope of the fit was 1 into the uncertainty intervals (0.93 ± 0.11, SD = 0.774). As expected, the independent term had not any statistical significance (7±10). The residuals for this fit were homogeneously scattered. This fact

demonstrates that there are no systematic differences in the obtained results for both elements. It is possible to conclude that the recoveries for both Tc and Re are the same. Therefore, using the method here proposed, it would be possible to calculate the Tc concentrations through the chemical yields for Re.

It is of interest to consider whether or not there are any systematic differences between the result precisions generated by the use of the different chemical yield tracers. For every replicate, the relative recovery uncertainties calculated using ^{95m}Tc were in the range of 1.2-1.6 %. Those values calculated using Re were in the range of 2.7-4.3 % (after excluding two values with high RSD values, which were due to some fluctuation on plasma conditions). This range of variation is higher than those calculated using the radioactive tracer. It seems that the Re-calculated recoveries showed a systematically larger uncertainty by a factor of 2-3. Therefore, it would be expected that the calculation of Tc concentration using the Re recovery could introduce larger total errors than those Tc concentrations calculated using the corresponding ^{95m}Tc recovery. However, the usual RSD values for Re recovery are in a low range. Therefore, this limitation would not be a major problem for those analyses avoiding the use of radioactive isotopes.

3.2. Technetium concentrations in the seaweed samples.

Table 3 also shows the Tc concentrations in the samples. These concentrations were calculated using two different ways. For the first approach, we used the recoveries calculated with ^{95m}Tc (2nd and 4th columns). In the second one, the recoveries obtained from Re were used (3rd and 5th columns).

As mentioned above, the results from a recent intercomparison exercise for ^{99}Tc in seaweed samples show that those laboratories that used Re as a chemical yield tracer systematically underestimated the Tc concentrations [18]. This fact could be due to a dissimilar fractionation of Tc and Re throughout the applied separation schemes. On the contrary, we show in table 3 that the obtained results using the methods described in the previous paragraph, were the same for both of them into a 1σ -uncertainty interval. There were four sample replicates for which the coincidence was produced into an interval of 2σ . A linear regression fit of the obtained ^{99}Tc concentrations for both calculation ways was then generated. The slope of the curve is 0.98 ± 0.01 . This fact shows that there is no systematic underestimation of Tc concentrations when Re is used in this method as a chemical yield tracer for Tc, when a confidence interval of 95% is considered.

The relative individual uncertainties of those results calculated using $^{95\text{m}}\text{Tc}$ were in the range of 2-16%, with an average value of 4%. For those results calculated using the Re recovery, the RSD values varied over a range of 4-20%, and the average value was 6%. This means that the major uncertainty sources in the results arise from the ICP-MS counting conditions with the samples.

We conclude that the differences in precision previously obtained for chemical recoveries were smoothed through the concentration calculations.

The distributions for Tc concentrations showed relatively good homogeneity between replicates. The average value varies very widely among the samples, because the Tc

concentration in the seaweed was dependent on the Tc concentration in seawater, which was not constant with time. The range of concentration distributions was very narrow. This fact reflected in the values of RSD for each sample; those values were in the range of 2-6 % for the other samples, except for the sample 3015, which showed 13%. When the concentrations were calculated using the chemical recovery of Re, the RSD values were in the range of 4-7 % (11% for sample 3015).

Concerning the differences in result distributions, and according to Table 3, the average values were the same using both methods. Therefore, it is possible to use this method for the analysis of ^{99}Tc using Re as tracer, without introducing systematic underestimation or overestimation of the Tc concentrations.

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Table captions.

Table 1. Chemical yields of Tc by three different separation methods (recovery $\pm 1 \sigma$ counting error). ^a Leaching performed using 4M HNO₃ after 30 minutes ashing ^b Leaching performed using 4M HNO₃ after 90 minutes ashing ^c Leaching performed using 8M HNO₃ after 90 minutes ashing.

Table 2. Operating conditions of ICP-MS.

Table 3. Chemical yields for ^{95m}Tc and Re, and Tc concentration values for the samples used in this work. ^a Values are determined using the chemical recovery of ^{95m}Tc. ^bValues are calculated using the chemical recovery of Re. Average ± 1 standard deviation, n = 5.

Sample	Date of collection	Method A ^a	Method B ^b	Method C ^c
3014	2000/01/11	78 ± 1	85 ± 1	88 ± 1
3015	2000/02/11	76 ± 1	89 ± 1	94 ± 1
3016	2000/03/13	70 ± 1	87 ± 1	89 ± 1
3017	2000/04/13	72 ± 1	91 ± 1	95 ± 1
3021	2000/08/16	88 ± 1	91 ± 1	90 ± 1

Table 1

Table Operating Conditions for ICP-MS

RF power	1340 W
Plasma gas flow rate	15 L/min
Auxiliary gas flow rate	1.0 L/min
Carrier gas flow rate	1.2 L/min
Solution uptake rate	0.2 mL/min
Sampling cone aperture (Ni)	1 mm
Skimmer aperture (Ni)	0.4 mm
Nebulizer type	Babington
Isotopes	⁹⁵ Mo, ⁹⁸ Mo, ⁹⁹ Tc, ¹⁰¹ Ru, ¹⁰² Ru, ¹⁸² W, ¹⁸⁵ Re, ¹⁸⁷ Re, ¹¹⁵ In (Internal standard)
Dwell time for ⁹⁹ Tc	45 ms
Dwell time for Re isotopes	9 ms
Sampling points per mass	3
Sweeps per replicate	1000

Number of replicates 4

Table 2.

Sample and replicate	^{95m} Tc recovery (%)	Re recovery (%)	⁹⁹ Tc ^a (Bq/kg d.w.)	⁹⁹ Tc ^b (Bq/kg d.w.)
3014	76.6 ± 1.1	79.0 ± 3.3	442 ± 10	429 ± 20
	97.9 ± 1.4	98.0 ± 3.3	442 ± 10	442 ± 16
	96.0 ± 1.5	93.2 ± 3.6	423 ± 11	463 ± 20
	93.1 ± 1.4	98.0 ± 3.9	453 ± 10	398 ± 17
	87.5 ± 1.1	96 ± 11	432 ± 9	394 ± 44
3015	90.0 ± 1.1	95.6 ± 3.6	431 ± 9	406 ± 17
	92.7 ± 1.4	90.3 ± 3.2	338 ± 8	369 ± 14
	97.1 ± 1.5	99.5 ± 2.7	316 ± 11	303 ± 12
	99.1 ± 1.5	99.1 ± 3.8	336 ± 8	336 ± 14
	93.7 ± 1.2	93.3 ± 3.7	379 ± 7	381 ± 16
3016	81.4 ± 1.1	80.2 ± 2.6	456 ± 13	406 ± 17
	96.1 ± 1.4	98.3 ± 4.4	474 ± 10	464 ± 22
	99.0 ± 1.5	102.6 ± 3.3	459 ± 12	443 ± 17
	95.8 ± 1.5	96.3 ± 3.3	462 ± 10	440 ± 16
	89.3 ± 1.2	92.2 ± 3.2	465 ± 11	450 ± 18
3017	81.9 ± 1.1	84.7 ± 2.4	454 ± 27	423 ± 27
	96.7 ± 1.4	99.3 ± 3.3	470 ± 10	458 ± 17
	94.4 ± 1.5	92.0 ± 3.3	464 ± 10	491 ± 19
	94.5 ± 1.5	97.1 ± 2.9	493 ± 12	469 ± 16
	94.8 ± 1.2	91.5 ± 3.9	483 ± 9	501 ± 22
3021	98.1 ± 1.1	100.2 ± 3.0	271 ± 6	265 ± 10
	98.1 ± 1.4	95.6 ± 3.7	269 ± 42	276 ± 43
	98.4 ± 1.6	95.1 ± 4.1	255 ± 6	274 ± 13
	94.4 ± 1.5	110 ± 14	301 ± 45	250 ± 49
	90.0 ± 1.2	92.7 ± 3.6	264 ± 6	256 ± 11

Table 3

Figure captions.

Figure 1: Fit of Tc activity concentration according to their calculations by two methods: with the recovery of ^{95m}Tc and with the recovery of Re.

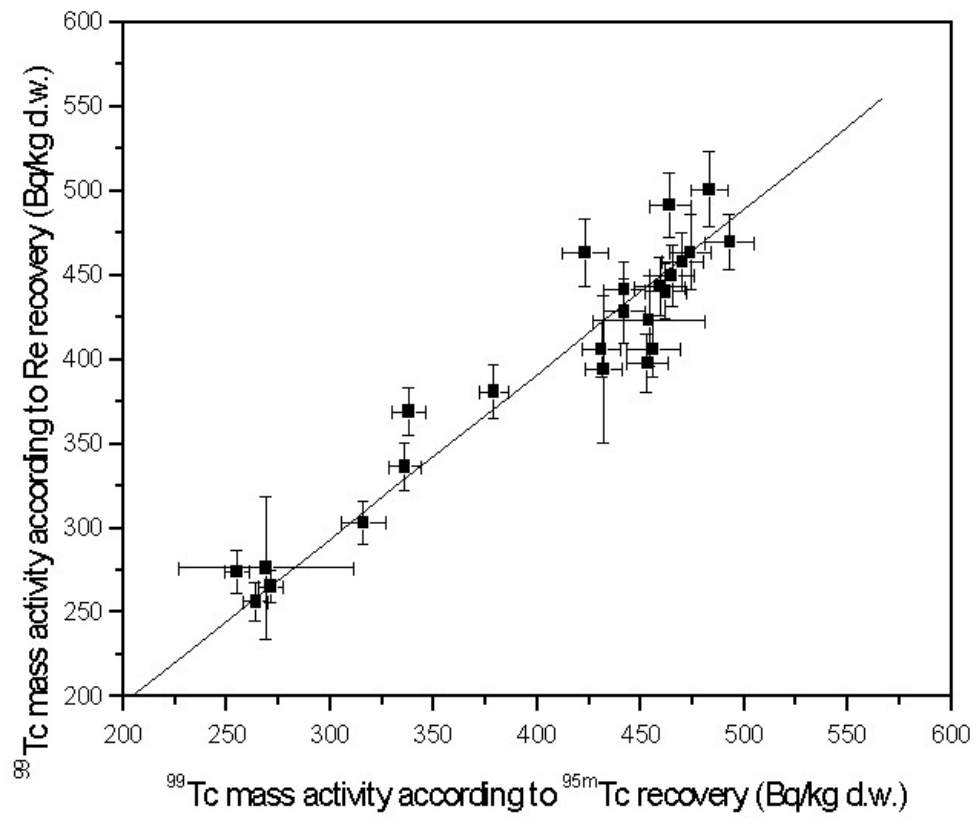


FIGURE 1.

