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Rapid sample purification approach for ³H determination in seawater using ion exchange resin

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Introduction: Tritium exists in the environment primarily in the form of tritiated water (HTO). There is a significant correlation between the radioactive levels of tritium in seawater and the safety of seafood. By accurately and rapidly detecting the tritium activity concentration in seawater, it is possible to effectively assess its potential impact on the seafood supply chain. At present, the detection of tritium in environmental water samples is often by liquid scintillation counting (LSC). To enable the measure of tritium by LSC, sample purification is necessary, which is commonly performed by distillation. The sample purification by distillation method is somewhat time consuming, especially when processing many samples or large volumes.

Methods: To improve the analytical efficiency in tritium determination, a method for the purification of tritium in seawater using ion exchange resin was developed in this work, which is highly suitable for large-scale environmental monitoring in emergency situations as it significantly shortens the sample processing time (A sample can be purified in 10 min, and multiple samples can be processed simultaneously, which is at least 50 min shorter than the distillation method). The influence of the ⁹⁰Sr-⁹⁰Y on the detection of tritium in seawater treated with ion-exchange resin was also discussed. The removal of metal ions from the seawater was achieved using magnetic agitation and filtration by mixing the sample with ion exchange resins.

Results: The results show that the ion exchange resin can effectively remove metal ions from seawater, and reduce the conductivity of seawater to< $1 \,\mu$ S/cm, and effectively reduce the influence of the 90 Sr- 90 Y on tritium detection. The method was validated using spiked samples and compared with other methods.

Discussion: The recovery of tritium for standard solutions treated by ion exchange method ranged from 85.1% to 98.45%, indicating satisfactory efficiency in sample purification for tritium determination in seawater. 10 seawater samples were collected and used to verify the applicability of the method.

KEYWORDS

ion exchange resin, purification, seawater, determination, tritium

1 Introduction

Tritium (³H, $t_{1/2}$ =12.3 y) is a radioisotope of hydrogen that is a pure β -decay particle. Tritium is produced both naturally and by human nuclear activities (Kaizer et al., 2023; Oms et al., 2019; Wallova et al., 2020). During the operation of nuclear power plants, waste water containing radioactive substances is inevitably discharged into the environment, among which tritium is one of the primary radionuclides (Adam-Guillermin et al., 2010; Guo et al., 2020; Köllö et al., 2010; Liang et al., 2022). The Japanese government has begun dumping contaminated radioactive wastewater from the Fukushima Daiichi Nuclear Power Plant (FDNPP) into the ocean on Aug. 23, 2023, which contains a large amount of tritium (Subban and Gadgil, 2019). After the discharge of nuclear wastewater or sewage into the sea (Dallas et al., 2016), tritium can be rapidly incorporated into marine organisms either by uptake from seawater or by food ingestion (Alava and Gobas, 2016; Madigan et al., 2012; Yankovich et al., 2011), thereby enters the human body through the food chain. Tritium can pose a health risk if ingested through drinking water or food, inhaled in the respiratory tract, or absorbed through the skin (Butler and Leroy, 1965; Matsumoto et al., 2021). Although tritium belongs to the low radiotoxicity group (Buesseler, 2020; Iryna, 2017; Men, 2021), once entering into human body, tritium may lead to long-term radiationinduced oxidative damage to cells (Gagnaire et al., 2020; Li et al., 2021; Rozhko et al., 2016), genotoxic and reprotoxic effects (Adam-Guillermin et al., 2012; Wakeford, 2014; Wanigaratne et al., 2013), and damages of DNA (Hatano et al., 2022).

There is a close connection between the radioactivity of seawater and seafood safety, as tritium produced by nuclear power plants can affect the safety of seafood through the food chain. Marine organisms absorb and accumulate tritium from their environment during their growth, and this accumulation effect can lead to tritium concentrations in seafood that are higher than those in the surrounding water. Monitoring tritium activity concentration in seawater can help identify and assess potential sources of contamination in a timely manner, allowing for appropriate measures to reduce or eliminate the impact of tritium on the environment and human health. This is essential for ensuring that the public can safely utilize seawater and consume seafood from the ocean. Therefore, method establishment for effective determination of tritium in seawater is important for radioanalytical experiment involved in nuclear emergency preparedness and environmental monitoring.

The liquid scintillation counting (LSC) is the most used method for its detection. Chemical and color quenching are typical challenges encountered when using LSC for sample measurement. In general, removing impurities from environmental water samples is necessary to reduce the chemical quenching for a highly precise tritium analysis using the liquid scintillation counting method. Therefore, to ensure accurate detection of tritium by LSC, effective impurities removal becomes extremely important. Standard procedures for the purification of tritium in water samples are usually performed by distillation (Varlam et al., 2009). However, the distillation process is time-consuming (Sakuma et al., 2012). In addition, the distillation process may result in isotopic fractionation between tritium and hydrogen during the evaporation process, introducing bias in tritium measurement (Atkinson et al., 2014).

With regards to water purification, several methods have been reported including reverse osmosis, filtration, ion exchange and distillation etc. Among which, ion exchange is widely used for water softening, pure water production (Iourtchouk and Bergmann, 2012; Lee et al., 2020), wastewater purification and seawater desalination (He et al., 2020), owning some attractive advantages, such as fast reaction kinetics, low cost, and high reliability (Ma et al., 2019; Subban and Gadgil, 2019). However, there are only some reports on the purification of tritium from seawater by ion exchange resin, and the results obtained are different according to the types of resin used, and there is a certain gap in the recovery rate of tritium standard solution (Nakasone et al., 2021; Tarancón et al., 2010).

For environmental-level seawater samples, even after purification, the low concentrations of HTO and significant dilution of regular water still make the direct measurement of tritium by LSC difficult (Janković et al., 2012). For such cases, further concentration of tritium with e.g., electrolytic enrichment, is needed (Garbarino et al., 2009; Groning et al., 2009; Kumar et al., 2016), while high purity of water sample is also required before the concentration treatment.

This study aims to develop an improved and rapid method for the determination of tritium in seawater samples by LSC after purification using ion exchange resin. In this study, several ion exchange resins were screened and performances for seawater purification were investigated. The accuracy of the method was validated using spiked samples and the results were compared with the traditional atmospheric distillation method. The method performance was evaluated using parameters of recovery, precision, and trueness.

2 Experimental

2.1 Selection of resin

The selected ion exchange resin for seawater adsorption should possess appropriate selectivity, rapid exchange rate, high exchange capacity, and resistance to physical rupture. Additionally, it should be easy to regenerate and economically affordable. In this work, 5 commercially available and inexpensive resins were selected for purification of seawater. Listed in Table 1 of 5 kinds of typical characteristics of ion exchange resin, and the water purification tests. As electrical conductivity is a straightforward indicator for the purity of a liquid solution, thus we utilized the changes of electrical conductivity before and after sample purification to evaluate the efficiency of matrix elements removal from seawater. The electrical conductivity of seawater collected from the South China Sea, the waters near the Republic of Kiribati, the sea near the Mariana Trench, the western Pacific Ocean and the Southwestern Indian Ocean ranges between $3 \times 10^4 - 6 \times 10^4 \mu$ S/cm (Zheng et al., 2018).

In order to select the appropriate resin, to 20 mL of seawater, 5, 10, 11, 12, 13, 14, 15 or 20 g of MB-20, MB-106UP, MB-450, T-42 or CH-99 resin was added and mixed in a beaker for 5 min with

Name	Manufacturer	Туре	Matrix structure	Functional group	lonic form supplied	Loading capacity, meq/mL
MB-106UP	Tulsimer®	Strong acid Cation Cross exchange resin linked polystyrene		Sulfonic acid	Hydrogen	1.8
		Strong base Anion exchange resin	trong base Anion exchange resin		Hydroxide	1.0
СН-99	Tulsimer [®]	Boron selective adsorption resin	Cross linked polystyrene	Poly hydroxy amine	Chloride	0.8
T-42	Tulsimer [®]	Strong acid Cation exchange resin	Cross linked polystyrene	Sulphonic	Hydrogen	1.8
MB-20	MB-20 AmberLite TM Strong acid Cation exchange resin divinylbe copoly Strong base Anion exchange resin		Styrene- divinylbenzene	Sulfonic acid	Hydrogen	1.0
			copolymer	Quaternary ammonium	Hydroxide	1.9
MB-450	AmberLite TM	Strong acid Cation exchange resin	Styrene- divinylbenzene	Sulfonic acid	Hydrogen	≥2.0
		Strong base Anion exchange resin	copolymer	Quaternary ammonium	Hydroxide	≥1.1

TABLE 1 Typical characteristic of the 5 types of resins selected in this work.

stirring. The seawater sample was filtered through a 0.22 μ m hydrophilic filter (Polytetrafluoroethylene, diameter of 13.00 mm, Shanghai Anpu Experimental Technology Co., Ltd.) and its conductivity (Seven Excellence, METTLER TOLEDO) was measured. The resin that can significantly reduce the conductivity of seawater was selected for subsequent experiments.

2.2 ICP-OES measurement

Inductively coupled plasma optical emission spectrometry (ICP-OES, ICAP PRO, Thermo Scientific) was mainly used to determine the content of metal ions in solutions. To compare the changes in the types and contents of metal ions before and after purification of seawater, ICP-OES was used to measure metal ions in seawater treated with MB-20 resin, MB-106UP resin, MB-450 resin, and atmospheric distillation after dilution for 100-fold.

The measurement of 27 metal ions such as Ca, K, Na, Mg, Cu, Mn, Fe and Zn in seawater were performed under the following operating conditions: air/acetylene flow of 13.50/2.00 L min⁻¹; burner height and still width of 13.5 and 0.2 - 1.0 mm; lamp current of 4-10 mA. The wavelengths and detection limits of 31 metal ions are shown in Table 2. Moreover, calibration curves were prepared from standard solutions of each metal with linear correlation of determinations above 0.999.

2.3 EDS, SEM and XPS

Energy dispersive spectrometer (EDS, X-max 50, OXFORD), scanning electron microscopy (SEM, Sigma 300, ZEISS) and X-ray photoelectron spectroscopy (XPS, K-Alpha, Thermo Scientific) were performed for the resin material before and after the purification process. To prepare the processed resin material, 15 g of MB-20, MB-106UP or MB-450 resin was mixed with 20 mL of seawater in a beaker and stirred with a on a magnetic stirrer for 30 minutes. After filtering the mixture through a 0.22 μ m filter, the resin was dried in an oven at 60°C for 5 h. 5g of dried ion-exchange resin and unused resin were ground into uniform powder samples, respectively, and then used for EDS, SEM, and XPA detection.

2.4 Conditions for screening

- 1. 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, and 15 g of MB-20 resin and 20 mL of seawater were magnetically stirred for 5 min. The conductivity was measured and recorded, and the experiment was repeated 3 times.
- 2. The mixed samples of 9, 10, and 11 g of resin with 20 mL of seawater were magnetically stirred, and the electrical conductivity was measured at 1, 2, 3, 4, 5, 10, 15, 20, and 30 min, respectively.

2.5 Method verification

2.5.1 Comparison of recovery rate

In this study, 3 spiked samples with tritium concentrations of 5.1, 51 and 102 Bq/L were prepared by spiking different amount (0.25, 2.5 and 5 mL) of a tritium standard solution (1022 Bq/g, the expanded uncertainty is 3.5%, k = 2, Chinese Academy of Metrology, No. DLhd2021-13,611) into a 500 mL volumetric bottle and seawater was added to the constant volume.

To 20 mL of spiked sample, 11 g of MB-20 resin was added and then magnetic stirring for 10 min. After filtering the sample through

lon	Wavelength, nm	Detection limits, μ g/mL	lon	Wavelength, nm	Detection limits, µg/mL
Sb	217.58	0.005	Tl	190.86	0.002
Ва	455.40	0.002	Ni	231.60	0.002
Bi	223.06	0.029	К	766.49	0.009
Cd	214.43	0.001	Na	588.99	0.009
Ga	396.85	0.009	Al	167.08	0.009
Cr	283.56	0.001	Sr	407.77	0.002
Со	238.89	0.001	Ti	334.94	0.010
Cu	324.75	0.001	Sn	189.99	0.004
Ca	393.37	0.009	V	309.31	0.001
In	230.60	0.008	Y	371.03	0.001
РЬ	340.45	0.005	Zn	213.85	0.001
Li	670.78	0.002	Zr	343.82	0.002
Mg	279.55	0.005	Ве	313.04	0.003
Mn	257.61	0.001	В	249.77	0.015
Мо	202.03	0.002	Fe	259.94	0.002
As	189.04	0.001			

TABLE 2 Wavelength and detection limit of metal ions detected by ICP-OES.

a 0.22 μ m filter, the sample was measured for tritium by LSC. To ensure the reliability of the results, the experiment was repeated four times for each group of spiked samples.

In addition, 3 groups of spiked samples were processed by atmospheric pressure distillation in the experiment. The specific operation is as follows: add 30 mL spiked sample, appropriate amount of zeolite and 0.05 g potassium permanganate to the distillation flask for distillation, and collect the middle distillate. To ensure the reliability of the results, four repeated experiments were carried out for each group of spiked samples.

2.5.2 Effects of 90 Sr-90 Y

0.5 mL tritium standard solution with a concentration of 10 Bq/ g and 4 mL 90 Sr- 90 Y standard solution (9.87 Bq/g, the expanded uncertainty is 3.0%, k = 2, Chinese Academy of Metrology, RYSR90180726-01) with a concentration of 0.28 Bq/g were respectively taken into 100 mL volumetric bottles, and water was added for constant volume. The activity concentrations of tritium and 90 Sr- 90 Y in the mixed solution were 50 Bq/L and 11.2 Bq/L, respectively. The solution was evenly divided into 3 parts, two of which were treated with atmospheric distillation and ion exchange in accordance with section 2.5.1.

2.6 Application of the method

To test the applicability of the developed method, 10 seawater samples were collected around Hangzhou Bay, Zhejiang Province, China on August 27, 2023. To compare the performance, each seawater sample was purified by both ion exchange resin and distillation method, followed by electrolysis enrichment as detailed below.

2.6.1 Ion exchange method

Seawater was mixed with the optimum resin and the ratio in a beaker and stir continuously with a magnetic stirrer for 10 min. The solution was separated from the resin with 0.22 μ m filter membrane. 500 mL of filtered sample was taken and placed it into the electrolytic enrichment device, and electrolyzed for 60 h to enrich tritium. After electrolysis was complete, the obtained solution was transferred into a glass bottle and sealed for LSC measurement.

2.6.2 Atmospheric distillation

700 mL of seawater, zeolite and 0.2 g potassium permanganate were added to the distillation flask, and distillation process was repeated for several times until the conductivity of obtained sample was < 5 μ S/cm (a single distillation process required about 12 h). 500 mL of condensed sample solution was taken and proceed with electrolysis as described above to enrich tritium.

2.6.3 Electrolysis enrichment factor

 $50~\mu L$ tritium standard solution (10.2 Bq/g) was diluted with background water a final volume of 500 mL, and proceed with electrolysis as described above to enrich tritium. The enriched tritium solution was measured by LSC to determine electrolysis enrichment factor.

2.7 Measurement of tritium by LSC

8 mL of enriched tritium fraction after electrolysis or background water or samples of standard solutions containing tritium was placed in a 20 mL polyethylene scintillation vial, and mixed with 12 mL of Ultima Gold LLT scintillation cocktail (PerkinElmer). The tritium activity concentration in the sample was determined by low-level LSC (Quantulus GCT 6220/Quantulus 1220, PerkinElmer), with energy range between 0 and 5 keV, and counting time of 1000 min. The radiochemical procedure is illustrated in Figure 1.

2.8 Tritium activity concentration

The tritium activity concentration in the enriched sample after electrolysis was calculated according to the following equation:

$$C = \frac{N_c - N_b}{0.06 \times m \times E \times n_c} \tag{1}$$

Where *C* is the tritium activity concentration in the enriched sample after electrolysis (Bq/L), N_c is the count rate of the enriched sample (cpm), N_b is the count rate of the backgrand (cpm), *m* is the weight of the sample contained in the counting vial, *E* is the counting efficiency of LSC for tritium, and η_e is the electrolysis enrichment factor.

The electrolytic enrichment factor was calculated according to the following equation:

$$\eta_e = \frac{C_f}{C_i} = \frac{V_i \times A_f}{V_f \times A_i}$$
(2)

Where C_i , A_i and V_i are the activity concentration (Bq/L), activity (Bq) and volume (mL) of the working solution before the electrolysis enrichment, respectively. C_f , A_f and V_f are the activity concentration (Bq/L), activity (Bq) and volume (mL) of the working solution after the electrolysis enrichment, respectively.

2.9 Statistics

The activity concentration is calculated as shown in Equations 1 and 2. The data was processed using Excel 2019.

3 Results and discussion

3.1 Conditional screening

3.1.1 Resin selection

The tritium measurement using LSC method requires the sample solution to be salt-free, transparent and colorless to ensure high counting efficiency (Pourimani and Aghamohammadi, 2014; Tjahaja and Sukmabuana, 2012). Therefore, removing impurities is an essential step before the LSC measurement. Electrical conductivity is a straightforward indicator for water salinity monitoring (Subaer et al., 2021; Thorslund and van Vliet, 2020; Wilson et al., 2011). The results for the 5 resins used in the screening are shown in Figure 2. Among the 5 resins, MB-106UP, MB-20 and MB-450 resins showed the ability to reduce the conductivity of seawater. Referring to the characteristics of the 5 resins in Table 1, it shows that the strong acidic cation and strong basic anion mixed-bed exchange resin is more effective to remove ions from seawater. In the case of a certain amount of seawater and conductivity, the least amount of resin: was required for MB-20 resin, followed by MB-450.

3.1.2 ICP-OES

Seawater typically contains 96.5% of water, 2.5% of salt and small amounts of other substances, with the major metal ions including sodium, potassium, magnesium, and calcium (Mackenzie, 2024). The salinity of seawater was too high to be measured directly by ICP-OES, consequently, 100-fold dilution was performed for each sample prior to the measurement. Table 3 shows the composition of seawater determined by ICP-OES, before and after passing over an ion exchange resin (the figure shows only the detected metal ions, and the metal ions below the lower detection limit are not shown). The main metal ions detected in seawater were sodium, potassium and magnesium, and their contents were in the order of sodium > magnesium > potassium. All the 3 cation-anion mix-bed resins (MB-106UP, MB-20 and MB-450 resins) and atmospheric distillation process could remove magnesium, sodium and potassium ions in seawater, comparatively, the impurity removal rate is significantly higher by





ion exchanges resins than the atmospheric distillation, for the aluminum.

3.2 Microscopic characterization

3.2.1 SEM-EDS

To further study the effect of ion exchange resin treatment on ions in seawater, SEM was used to characterize the surface morphology of resin before and after seawater treatment, while EDS was used to analyze the changes of element content in resin before and after seawater treatment. The results are shown in Figure 3 and Supplementary Figures S1-S2 in Supplementary Material. The SEM scanning results show that the surface of the 3 kinds of resins has no obvious change before and after treatment of seawater, and it is smooth and uniform. It may indicate that the resin can be reused after elution treatment.

As shown in Figure 3 and Supplementary Figure S1, the contents of sulfur, chlorine, and carbon ions in the MB-20 and MB-106UP resins remained relatively stable after seawater treatment, with no significant changes observed. However, the

atomic percentages of sodium, potassium, and magnesium increased in both resins, specifically by 1.84%, 0.07%, and 0.25% in MB-20 resin, and by 0.08%, 0.02%, and 0.13% in MB-106 resin, respectively. As can be seen from Supplementary Figure S2, after treating seawater with the MB-450 resin, the levels of sulfur, chlorine, and sodium increased by 2.4%, 0.32%, and 0.03%, respectively, while other ions showed no significant changes.

3.2.2 XPS analysis

XPS was used to detect the elemental content in the resin before and after seawater treatment, and the results are shown in Figure 4 and Supplementary Figures S3-S4 in Supplementary Material. Through the modification of the external spectra of the three kinds of resin before and after the specific absorption of metal ions, the infrared spectra of the three types of resin before and after metal ion adsorption remain largely unchanged, and the position and shape of the main characteristic peaks change little, indicating that the skeletal structure of the resin does not undergo chemical reactions.

Comparisons were made regarding the exchange capacity and conductivity reduction ability of the three resins, and MB-106UP

TABLE 3 Concentration of metal ions in seawater before and after treatment with ion exchange resin or atmospheric distillation.

Method	Concentration, µg/mL				Removal rate, %				
	Sodium	Aluminum	Potassium	Magnesium	Sodium	Aluminum	Potassium	Magnesium	
Seawater dilution for 100-fold	2.704	<0.009	0.124	0.463	/	/	1	/	
MB-450	<0.009	<0.009	0.022	0.005	>99.997	/	>99.823	>99.989	
MB-106UP	<0.009	<0.009	<0.009	0.015	>99.997	/	>99.927	>99.968	
MB-20	<0.009	<0.009	<0.009	0.047	>99.997	/	>99.927	>99.898	
Atmospheric distillation	0.356	0.059	0.037	0.194	>99.868	*	>99.701	>99.581	

"*" It means that the zeolite added in the distillation process to prevent the solution from boiling contains aluminum, resulting in increased aluminum content in the distillation solution.



FIGURE 3

SEM images and EDS spectra of MB-20 resin before and after seawater treatment. (a) is the SEM image of MB-20 resin before seawater treatment, and Figures (b) and (c) are the EDS spectra of MB-20 resin before seawater treatment. (d) is the SEM image of MB-20 resin after seawater treatment, and Figures (e) and (f) are the EDS spectra of MB-20 resin after seawater treatment.

resin could not reduce the conductivity to below 5 μ S/cm. Under fixed seawater volume and conductivity conditions, the amount of MB-20 resin is the least. EDS results showed that MB-20 resin had stronger ability to adsorb metal ions and anions in seawater. After comprehensive evaluation of various relevant factors, MB-20 resin was selected as the best choice for seawater purification process in this study.

3.3 Condition optimization

3.3.1 Ratio of resin to sample

With the consideration of account, the loss of the sample during resin purification and to meet the measurement requirements of LSC, the seawater sample volume was set at 20 mL. The relationship between the seawater conductivity and the amount of resin added



was discussed when the sample size was 20 mL, and the optimal resin dosage was determined. As shown in the Figure 5, under the condition that the seawater sample volume is set to 20 mL and the reaction time is set to 10 min, when the resin dosage was within the range of 5 to 10 g, it was observed that the seawater conductivity gradually decreases with the increase of the resin addition amount. However, when the resin dosage is 11 g, the seawater conductivity drops below 1.5 μ S/cm, and with further increases in resin dosage, no significant change in seawater conductivity was observed.

3.3.2 Relation between electrical conductivity and stirring time

To investigate the effect of different magnetic stirring durations on seawater conductivity, mixed samples containing 9, 10, and 11 g of resin and 20 mL of seawater were prepared. As shown in Figure 6, when 9 g of resin was added, the conductivity of seawater gradually decreased with the extension of stirring duration and stabilized at 1.6 μ S/cm after 20 min. When 10 g of resin was added, the seawater conductivity decreased gradually within 15 min of stirring, after which it remained constant at 0.9 μ S/cm. With 11 g of resin, the seawater conductivity decreased within 10 min, and after that, it stabilized at approximately 0.9 μ S/cm.

To optimize efficiency and cost-effectiveness, the dosage of resin and mixing time were comprehensively analyzed and compared. The results indicate that optimal reaction efficiency and economic benefits can be achieved when the amount of seawater is 20 g, the resin dosage is 11 g, and the stirring time is 10 min. There is a big difference in purification time between ion exchange and atmospheric distillation, and the results are shown in Table 4. Atmospheric distillation took a long time to purify the samples (about 24 h), and the sample recovery was 75.71 - 86.89%. The ion exchange purification process was simple, taking about 10 min, and the sample recovery was 85.71%.

3.4 Method verification

To verify the accuracy of the method, spiked samples with three different tritium activity concentrations (5.1, 51 and 102 Bq/L) were

purified and measured. The recoveries were calculated according to the ratio of the tritium activity concentration of the treated seawater to that of the standard solution prepared before the treatment. As shown in Table 5, the recoveries of tritium treated by MB-20 resins were all above 85%, within the ranges of 85.12 - 98.45%. Keisuke Soga et al. used distillation method to treat tritium as tissue free water in food, and the recovery was higher than 75% (Soga et al., 2016). Shunya Nakasone, et al. used ion-exchange resin to treat tritium in river water, and the recovery ranged from 77% to 111% (Nakasone et al., 2021). Our results are comparable to those reported earlier, demonstrating the accuracy of the developed method.

To consider the influence of ⁹⁰Sr-⁹⁰Y on the experiment, the mixed solution samples containing tritium and $^{90}\mathrm{Sr}\text{-}^{90}\mathrm{Y}$ with a certain concentration were prepared in this study and tested by LSC. The tritium recovery of the three samples within low energy wide channel were shown in Table 6. ⁹⁰Sr-⁹⁰Y contributed little to the tritium detection count rate in the low energy wide channel, and there was little difference in the tritium recovery between the samples before treatment and the samples after ion exchange or atmospheric distillation. The spectrogram of LSC of tritium is shown in Figure 7. Before the measurement wide channel of 200, there is no significant difference between the sample spectra before treatment, ion exchange treatment and atmospheric distillation treatment. When the measurement width was 300 - 900, the peak of the samples before treatment was significantly higher than that after MB-20 resin and atmospheric distillation, indicating that both atmospheric distillation and MB-20 resin could remove 90Sr-90Y from water.

3.5 Application of the method

For environmental-level seawater sample analysis, due to its low tritium concentration, direct measurement using LSC is still challenging (Muranaka et al., 2011). The International Atomic Energy Agency recommends the addition of an electrolytic concentration pretreatment, which can significantly reduce the





TABLE 4 Purification of seawater samples by ion exchange resin and atmospheric distillation.

Number	Index	lon exchange resin	Atmospheric distillation		
			Once	Twice	
1	Time of processing, min	10	720	1440	
2	Amount of sample, mL	700	700	700	
3	Sample recovery rate, %	85.71	87.14	75.71	

detection limit of the liquid scintillation to accommodate measurement of tritium in the environment (Plastino et al., 2007; Saito, 2008; Satake and Takeuchi, 1991). To further verify the feasibility of this method, 10 seawater samples were collected and treated with MB-20 resin and atmospheric distillation respectively. Table 7 shows the activity concentration and standard deviation of tritium in different seawater. The tritium activity concentrations in seawater treated with ion-exchange resin and atmospheric distillation were respectively 1.30 ± 0.35 Bq/L and 1.58 ± 0.32 Bq/ L. Calculating the uncertainty of each test result increases the reliability of the results. The results are shown in Table 7. The two methods have good consistency in the detection of tritium in seawater. For the purification of tritium activity concentration in each seawater sample, the ion exchange resin method took a total of 10 min, and the atmospheric distillation method took a total of >24 h (two or more distillation treatments). In summary, the detection results of tritium in seawater treated by ion exchange resin are comparable to those by distillation method, and the sample treatment time is 1/144.

When measuring low-level environmental samples, electrolysis enrichment would be necessary prior to LSC measurement, therefore, large volume (200 - 500 mL) of seawater should be purified, and accordingly the amount of resin required also increases. To ensure cost-effective, green and sustainable development, the team will consider re-using ion exchange resins in the future.

TABLE 5	Comparison	of tritium	recovery	for	spike	sample	prepared	with	ion	exchange	and	distillation
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Sample, Bq/L	Method	Range, %	x ± S, %	RSD, %
5 1	Atmospheric distillation	97.74~112.80	105.15 ± 7.53	7.17
5.1	MB-20	85.12~88.80	87.52 ± 2.07	2.37
	Atmospheric distillation	102.57~106.51	105.07 ± 2.18	2.07
51	MB-20	90.87~98.45	94.25 ± 3.13	3.33
102	Atmospheric distillation	92.90~97.20	95.29 ± 2.19	2.30
102	MB-20	92.43~96.83	96.61 ± 3.37	2.23

TABLE 6 Effect of ⁹⁰Sr-⁹⁰Y on tritium detection.

Sample, Bq/L	Method	Activity concentrations <u>+</u> U (k=2), Bq/L	Recovery, %
	Before treatment	53.58 ± 0.02	107.17
50	MB-20	48.56 ± 0.10	97.13
	Atmospheric distillation	51.96 ± 0.13	103.92

4 Conclusions

With the rapid development of nuclear technology, it is necessary to monitor tritium levels discharged into the sea from nuclear power plants. In this study, a rapid method was developed using MB-20 ion exchange resin followed by LSC measurement for determining tritium in seawater. The accuracy of the developed method was confirmed by analyzing spiked samples. The distinct advantage of the developed method is its significantly reduced analytical time compared to the traditional method. Particularly, it is suitable for environmental monitoring, especially under emergency situations. The results show that MB-20 resins have good adsorption effect on metal elements in seawater, and can rapidly reduce the content of sodium and potassium in seawater, and then reduce the conductivity of seawater (less than 1 μ S/cm). The recoveries of the tritium standard liquid treated by ion exchange method were 85.12 - 98.45%, and those treated by atmospheric distillation method were 92.90 - 112.80%. In the field of radionuclide detection, especially in the detection process of tritium in complex samples such as seawater, environmental samples or nuclear facility emissions, it is particularly critical to effectively reduce the influence of other radionuclides on tritium detection. In this study, ion-exchange resin and atmospheric distillation were used to treat the mixed solution containing a



TABLE 7 Tritium activity concentrations in seawater.

Sample	lon exchang	e resin, Bq/L	Atmospheric d	istillation, Bq/L
1	1.24 ± 0.02		1.67 ± 0.02	
2	1.53 ± 0.02		1.39 ± 0.02	
3	1.35 ± 0.02		1.23 ± 0.02	
4	1.40 ± 0.02	1 20 + 0.25	1.08 ± 0.02	-
5	1.21 ± 0.02		1.70 ± 0.02	1.50 + 0.22
6	1.44 ± 0.02	1.30 ± 0.35	1.49 ± 0.02	1.58 ± 0.32
7	1.35 ± 0.02		1.58 ± 0.02	-
8	1.08 ± 0.03		1.57 ± 0.02	-
9	0.61 ± 0.03		1.68 ± 0.02	-
10	1.01 ± 0.03		1.60 ± 0.02	

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certain concentration of tritium and ⁹⁰Sr-⁹⁰Y, and the spectra and recovery of the mixed solution were compared. The results show that the ion-exchange resin can remove ⁹⁰Sr-⁹⁰Y from seawater very well, and the peak of the spectrum can be observed to decrease obviously, and the tritium recovery was 97.13%. The sample processing time of ion exchange method is short, only 10 min to complete the sample purification treatment, which significantly improve the analytical efficiency. Based on the above experiments, the purification of seawater by ion exchange resin has high recovery rate of tritium and short sample processing time. It is an efficient, rapid, simple and environmentally friendly sample processing method for tritium analysis in seawater, which can meet the existing needs.

In nuclear energy production, monitoring tritium - a radioactive isotope - is crucial for environmental and public health safety. Rapid and accurate measurement of tritium is vital for assessing environmental impacts and responding to emergencies at nuclear plants. This study's proposed sample treatment method enables swift tritium activity measurements in seawater, with the simplicity and ease for field application. Implementing this method will enhance emergency response efficiency and ensure timely monitoring of environmental radioactivity, thus safeguarding marine environments and human health from potential radioactive threats.

Data availability statement

The original contributions presented in the study are included in the article/Supplementary Material. Further inquiries can be directed to the corresponding author.

Author contributions

HR: Investigation, Writing – original draft, Writing – review & editing, Methodology, Funding acquisition. MX: Investigation, Writing – original draft, Writing – review & editing. PW: Funding acquisition, Methodology, Writing – review & editing. YS: Investigation, Writing – original draft. HZ: Investigation,

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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Supplementary material

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