Adsorption of Anionic Chloro Complexes of $^{59}\text{Fe}$ and $^{195}\text{Au}$ on Non-ionic Resins of Macro-reticular Type

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Received March 7, 1985

Adsorption behavior of $^{59}\text{Fe}$ and $^{195}\text{Au}$ on the non-ionic macro-reticular resin, Amberlite XAD-7 is studied. Distribution coefficients ($K_d$) for both nuclides in hydrochloric acid or lithium chloride solutions above 6M are particularly high. In nitric acid solution below 2M, $^{195}\text{Au}$ is highly adsorbed on the resin but $^{59}\text{Fe}$ is negligible over any concentrations. This resin did not adsorb other important radionuclides such as $^{54}\text{Mn}$, $^{60}\text{Co}$, $^{65}\text{Zn}$, $^{90}\text{Sr}$, $^{106}\text{Ru}$, $^{137}\text{Cs}$ and $^{144}\text{Ce}$ at all.

Based on such peculiar adsorption behavior, application to selective separation and determination of radio and stable iron in sea water was also studied.

Key Words: iron-59, gold-195, adsorption, macro-reticular resin, hydrochloric acid, lithium chloride, stable iron, sea water

1. Introduction

A new type of resinous adsorbents such as Amberlite XAD-2 and XAD-7, consists of non-ionic macro-reticular (MR) copolymer. Though they are originally developed as adsorbents for various organic matters in aqueous solutions, extrinsic use of the resins in inorganic analytical chemistry has recently been reported$^{[2]}$. That is, concentration of various transition metals or their radionuclides by adsorption on XAD resins can be performed, if they are converted to organic metal salts by treating them with suitable organic ligands. The adsorption may be due to formation of their organic complexes$^{[4]}$.

Since these resins have no ion exchange abilities, metal cations or complex anions of transition metals can not be expected to enter the resin matrix at all. Recently, however, it was preliminary reported by the authors that chloro complex anion of $^{59}\text{Fe}$ could be extremely adsorbed on XAD-2 and XAD-7 from hydrochloric acid or lithium chloride solutions without organic reagents$^{[5]}$.

The present report deals with details of the adsorption behavior of $^{59}\text{Fe}$ on XAD-7, and with the application for selective separation of $^{59}\text{Fe}$ from other radionuclides, and touches upon the determination of stable iron in sea water. Adsorption behavior of $^{195}\text{Au}$ which readily forms chloro complex anion in chloride solutions was also studied.

2. Experimental

2.1 Materials and apparatus

Amberlite XAD-2 is hydrophobic copolymer of styrene divinylbenzene and XAD-7 is hydrophilic acrylic esters. The 20 - 50 mesh portions were purified by washing with 1M sodium hydroxide, then with 1M hydrochloric acid and finally with methanol. The resins were dried in an open air before use.

Radioactive $^{59}\text{Fe}$ and $^{195}\text{Au}$, and other radionuclides supplied from Oak Ridge National Laboratory were prepared as 0.1M hydrochloric acid solution. Hydrochloric acid used was of super special grade (Wako Pure Chemical Industries, LTD.). All other chemicals were of
reagent grade.

Lithium chloride solution was acidified below pH 2.0 with hydrochloric acid before use. Lithium chloride solution used for the determination of stable iron in sea water was passed through XAD-7 column in order to eliminate Fe(II) before use.

Sea water was collected at 3.8 km off the coast of Ibaraki Prefecture, and was filtered through a membrane filter (0.45 μm) before use.

Activity was measured with a single channel pulse-height analyzer (Fuji Electric Co.) coupled with a well-type NaI(Tl) scintillation probe or with a 4096 channel pulse-height analyzer (CA-NBERRA) coupled with a well-type Ge(Li) detector.

Concentration of stable iron was measured by inductively coupled plasma spectrometer, JOBIN IVON JY38 (Daini Seikosha Co.).

A rotary shaker was used for agitation.

2.2 Procedures
All the experiments were performed at room temperature. Typical procedure was as follows. Ten ml of hydrochloric acid or lithium chloride solution containing 59Fe or 195Au was stirred with 0.1 g of XAD-7 in a glass conical beaker. After 3 hours' agitation, an aliquot (1.0 ml) of the supernatant solution was taken out with a pipette.

Adsorption percentage and distribution coefficient were calculated using the following equations:

adsorption percentage (\%) = \left\{ \frac{(C_0 - C)}{C_0} \right\} \times 100

distribution coefficient (Kd) = \left\{ \frac{(C_0 - C)}{C} \right\} \times \frac{\text{volume of the solution (ml)}}{\text{weight of the resin (g)}}

were \( C_0 \) and \( C \) are the activity concentrations of 59Fe or 195Au in the supernatant solution before and after agitation, respectively.

3. Results and Discussion

3.1 Adsorption of 59Fe and 195Au

Effect of agitation time on adsorption was firstly studied using 0.1 g of XAD-7 and 10 ml of 10M hydrochloric acid solution. Adsorption of both nuclides reached equilibrium within 1 hour.
Adsorption equilibrium of $^{59}$Fe and $^{195}$Au on XAD-7 from hydrochloric acid and lithium chloride solutions of various concentrations are shown in Fig. 1 and Fig. 2. The distribution coefficient ($K_d$) for $^{59}$Fe increased with increasing hydrochloric acid and lithium chloride concentration. However, $K_d$ for $^{195}$Au increased with increasing lithium chloride concentration but with decreasing hydrochloric acid concentration.

Majority of transition elements form anionic chloro complexes in hydrochloric acid solution and are adsorbed on an anion exchange resin. However, the work of Kraus, et al. showed that some negatively charged complexes such as FeCl$_4^-$, AuCl$_4^-$, GaCl$_4^-$, etc. were adsorbed characteristically by cationic resins. Adsorption of chloro complex anion of $^{59}$Fe and $^{195}$Au on XAD-7 was similar to that obtained with cation exchange resins by Kraus, et al.

For comparison with the behavior in chloride solution, adsorption of $^{59}$Fe and $^{195}$Au on XAD-7 from nitric acid solution were also studied. Results are shown in Fig. 3. The resins have high adsorption ability for $^{195}$Au below 2M nitric acid but not for $^{59}$Fe over any concentrations of nitric acid.

Interestingly, Fe(II) and Au(II) may also be extracted readily from hydrochloric acid and Au(III) from nitric acid by ethers, although the relation between the adsorption and the extraction is not clear.

Adsorbability for Amberlite XAD-2 was also studied. Adsorption of both nuclides on XAD-2 from hydrochloric acid solution is lower than that on XAD-7. This may be due to the hydrophobic property of XAD-2. However, adsorption of $^{195}$Au on XAD-2 is higher than that on XAD-7 in the higher acidity region of nitric acid concentration, probably became of high resistibility of XAD-2 to nitric acid concentration.

3.2 Applications

For the purpose of a practical application to analytical and radioanalytical chemistry, several experiments were preliminarily studied.

The effect of Fe(II) carrier on adsorption of $^{59}$Fe in 10M lithium chloride solution was examined. The distribution coefficient is $10^4$ to $10^5$ when the concentration of Fe(II) is lower than $10^{-3}M$, and decreased with increasing Fe(II) carrier concentration. Almost the same result was obtained with $^{195}$Au and Au(II) carrier.

Adsorption of radioiron from sea water was performed by spiking sea water with $^{59}$Fe. Effect of lithium chloride concentration on the adsorption is shown in Fig. 4. The adsorption of $^{59}$Fe in 10 ml of sea water on 0.1 g of XAD-7 was quantitative above 2.0 g of lithium chloride, and the time necessary to reach adsorption equilibrium was within 3 hours under continuous agitation.

The behavior was also confirmed by a column operation. When 2 l of sea water spiked with $^{59}$Fe was passed through a column of XAD-7 (1.0 cm diam., 10 cm height) at a flow rate below 1ml/min, the adsorption of $^{59}$Fe was quantitative. Adsorbed $^{59}$Fe could be eluted from the column with 1M nitric acid.

Based on these results, concentration of stable...
Iron in natural sea water was examined. Ten ml of concentrated hydrochloric acid and 2 l of 12M lithium chloride solution (iron removed) were added to 2.0 l of sea water. The treated sea water was passed through a column (2.0 cm diam., 30 cm height) of XAD-7 at a flow rate below 100 ml/h. The color of the top of the column changed from white to yellow, indicating the adsorption of Fe(III). The adsorbed iron was eluted with 200 ml of 1M nitric acid, and the concentration of iron in the effluent was determined at 258.90 mn by Inductively Coupled Plasma Spectrometry (ICP). Forty ppb of iron in sea water was obtained by the present method. No iron was detected in the solution passed through a column.

The behaviors of other important radionuclides, which are produced by the operation of nuclear plants and will eventually contaminate environmental samples, e.g. 54Mn, 60Co, 65Zn, 85Sr, 106Ru, 137Cs and 144Ce were examined. Then, 0.1 g of XAD-7 was shaken with 10M lithium chloride solution containing 59Fe, 60Co, 65Zn, 106Ru and 137Cs as tracers. The γ-spectra of the resin phase and the aqueous phase after treatment show that 59Fe selectively adsorbed, while other nuclides are not. 54Mn, 85Sr (to simulate 90Sr) and 144Ce were not adsorbed on the resin.

From the results obtained, it was shown that non-ionic macro-reticular resins could be used for rapid, simple and selective separation of 59Fe by converting the iron to chloro complex anion with hydrochloric acid or lithium chloride, with no organic reagents. This method can thus be effectively used for concentrating 59Fe and stable iron from a large volume of sea water.

References