

Development of functional resins by modification of ion-exchange resins and their application to analytical chemistry

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Abstract - Some novel functional resins were developed for highly selective separation and/or determination of mercury, selenium, fluoride and hydrogen peroxide, by simple modification of common ion-exchange resin with appropriate reagents. These reagents should have three functional properties, namely selective reaction with the determinant of interest, an ion-exchange reaction with the resin and physical adsorption on the ion-exchange resin matrix. These functional resins were applied to the analysis of some environmental water samples and satisfactory results were obtained.

INTRODUCTION

We have attempted to develop an useful method for the preparation of the functional resins for the separation and/or determination of the substances which are the target of analysis in environmental and biological chemistry, by a simple modification of ion-exchange resin with appropriate reagents. The reagents for this purpose should have three functional properties, namely selective reaction with the determinant of interest, an ion-exchange reaction with the resin and strong physical sorption on the ion-exchange resin matrix (Fig. 1).

Common ion-exchange resin could be converted into various kinds of functional resins only by mixing it with aqueous solution of the terfunctional reagent. The reagent is immobilized on the resin by the ion-exchange reaction and the physical adsorption, and does not release from the resin even in the presence of common ions with considerably high concentration. We have designed and synthesized proper molecules of the reagent which behave as the terfunctional reagent for the highly selective separation and/or determination of mercury, selenium, fluoride and hydrogen peroxide. The development of new functional resin is possible by the molecular design of the reagent without any difficulties in the synthetic procedure for the introduction of various functional groups in the resin. In addition, two possibilities can be taken into account in the elution of the substance adsorbed and the recovery of the resin (Fig. 1).

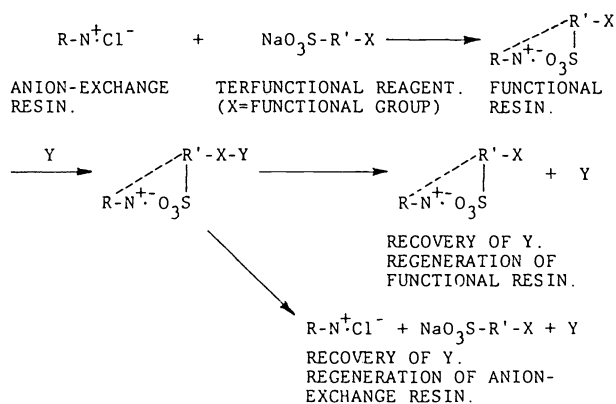


Fig. 1.
 Preparation and regeneration of anion-exchange resin functionalized with terfunctional reagent.

----- physical interaction

In some cases, the functional resin behaves as a catalyst and can be used repeatedly. The functional resins are applied to flow system. Furthermore, the substance adsorbed on the resin is stable and can be stored for a long time without any particular caution, hence the use of the functional resin is advantageous in the storage of the sample.

FUNCTIONAL RESINS FOR COLLECTION OF MERCURY

We have designed and synthesized two reagents (Fig. 2)(ref. 1 and 2) expecting proper terfunctional property for the separation of mercury, when the anion-exchange resin is loaded with these reagents. ATPS is the first example of the chelating agent that bears mercapto and azo groups as the chelating sites. We could not find out any valuable reagent as the terfunctional reagent in commercially available chelating agents (ref. 3). In the cases of some reagents, the physical adsorption onto the resin was not strong enough, and they leaked readily into the solution in the presence of chloride ion. In addition, in the cases of some reagents, the exchange capacity was not satisfactorily high, probably because they were too bulky to be held in the cavity of the ion-exchange resin. The exchange capacities for DzS and ATPS were found to be 1.9 mmol/g resin and 1.3 mmol/g resin, respectively. DzS and ATPS did not leak into the solution even in the solutions of 1 M NaCl, 0.5 M HCl and 1 M NaCl. On the contrary, in the case of dithizone, the amount immobilized on the resin was very small, because the contribution of the ion-exchange reaction is not available. Highly selective adsorption of mercury(II) was achieved at pH 1 - 7 without any leakage of ATPS from the resin in 0.5 M NaCl solution with distinct color change of the resin from red to yellow (Fig. 3). When the initial concentration of mercury(II) ion was 10 mg/l, ATPS resin could reduce that to 2 ng/l. The complete elution of mercury was achieved with 8 M nitric acid or 10 % thiourea solution in 0.1 M perchloric acid. The original anion-exchange resin was recovered when nitric acid was used, whereas the resin loaded with ATPS was recovered when thiourea was used. On the contrary, in the case of commercially available chelating agent used for the collection of mercury, regeneration of the resin is impossible, and the ignition of the resin which adsorbed mercury(II) is unavoidable for the final disposal of the resin; that may cause undesirable effect to the environment. The concentration of mercury(II) in the waste water can be reduced to that lower than the limit set by law in Japan by the use of this functional resin. The anion-exchange resin loaded with DzS is also effective similarly to that loaded with ATPS.

In conclusion, the functional resins prepared from ATPS and DzS with anion-exchange resin are regarded as valuable sorbent for the collection of mercury(II) in the treatment of waste water and also for the preconcentration in trace analysis of mercury(II).

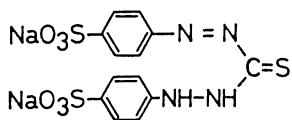
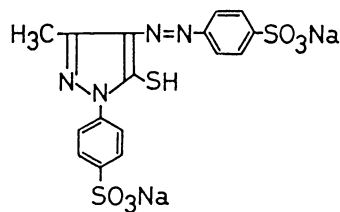


Fig. 2 dithizone sulfonic acid (DzS)



azothiopyrinesulfonic acid (ATPS)

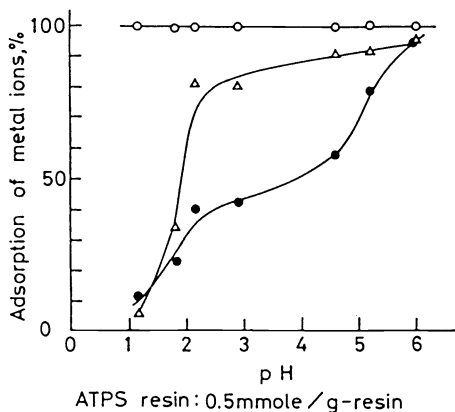
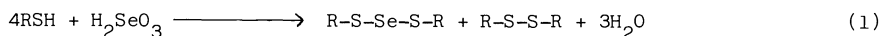


Fig. 3 Adsorption of mercury (II), copper (II) and cadmium (II) ions from 0.5 M NaCl solution by batch operation
Initial concentration: 10 mg/l ○ Hg(II)
△ Cu(II), ● Cd(II)

FUNCTIONAL RESINS FOR SEPARATION AND DETERMINATION OF SELENIUM

The biological activity of selenium has been of great interest since its recognition as an essential component of glutathione peroxidase (ref. 4). In addition, the role of selenium as a biological protector against highly toxic metals has been proposed (ref. 5). On the other hand, the pollution caused by selenium is a matter of concern in environmental protection, because of its high toxicity. The comparatively narrow concentration gap between the essential level and the toxic level demands the development of the methods for the accurate determination of low levels. Some sorbents for the collection of selenium have been proposed, but all are lacking in selectivity. We attempted to develop highly selective functional resins by the use of the terfunctional reagents which possess selective reactivity towards selenium. Formation of selenotrisulfide from selenium and thiol that has been presumed in the metabolism of selenium is regarded as a highly selective reaction of selenium. In an attempt to apply this reaction for the collection of selenium, we have investigated the reaction of selenium(IV) and various thiols. We found that ATPS, bismuthiol-II and penicillamine form very stable selenotrisulfides, while various other thiols form comparatively unstable selenotrisulfides. The formation of selenotrisulfide is expressed as in the reaction (1).



The anion-exchange resin loaded with ATPS was effective for the collection of selenium(IV) in acid medium. The maximum amount of selenium(IV) sorbed showed that the binding ratio of Se(IV) to ATPS on the resin was approximately 1:4, indicating that the reaction (1) took place on the resin. We have found that bismuthiol-II (Fig. 4) also reacts according to the reaction (1) and can be used to prepare a functional resin for the selective collection of selenium(IV). The exchange capacity for bismuthiol-II to the anion-exchange resin was found to be 3.1 mmol per g resin, which is comparable with that for chloride ion.

The release of bismuthiol-II from the resin was not observed even in 1.0 M sodium chloride solution, indicating that this reagent is immobilized on the resin by some physical interaction besides the ion-exchange.

The collection of selenium(IV) with the resin loaded with bismuthiol-II was complete at pH below 2, where most of the metal ions are unable to form chelate with bismuthiol-II. Bismuthiol-II can be adsorbed onto the resin with ion-exchange based on its thiolate group and physical adsorption, and in addition, thiolate group present on the resin becomes free in acid medium to react with selenium(IV). Accordingly, bismuthiol-II behaves as a terfunctional reagent. Selenium adsorbed could be eluted by penicillamine solution through the formation of extremely stable selenotrisulfide (ref. 6), and the eluted solution was applied to the determination by fluorimetry with diamionaphthalene (Fig. 5). This method gave satisfactory results on some environmental samples which contain 0.015 - 0.09 $\mu\text{g/l}$ selenium(IV). The formation of selenotrisulfide is only available for selenium(IV), and this reaction can be applied to the collection of selenium(VI) after its reduction to selenium(IV). We found that the boiling of the solution containing selenium(VI) with 3 M hydrochloric acid was enough for the reduction to selenium(IV) based on the observations in ion chromatography under various conditions. For the respective determinations of selenium(IV) and (VI), bismuthiol-II sulfonic acid (Fig. 6) was used instead of bismuthiol-II, because this reagent was found to be better than bismuthiol-II in its solubility and stability of selenotrisulfide formed. We established a procedure for the respective determinations of selenium(IV) and (VI) by the use of the resin loaded with bismuthiol-II sulfonic acid. Satisfactory results have been obtained on some sea water and estuarine water samples.

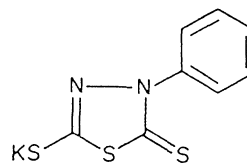


Fig. 4. Bismuthiol-II.

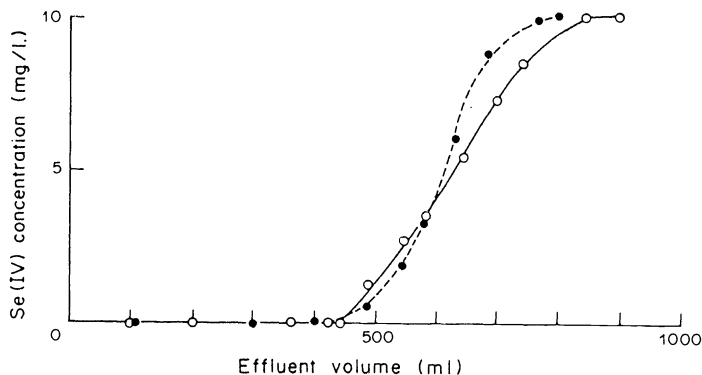


Fig. 5. Break-through curves for selenium(IV). Bismuthiol-II resin: (I) —○— 0.2 mmole/g, (II) ···●··· regenerated with 0.1M penicillamine at pH 5. Resin column 10 × 50 mm. Concentration of selenium(IV) in the sample solution 10 mg/l., in 0.3M hydrochloric acid. Flow-rate 40 ml/hr.

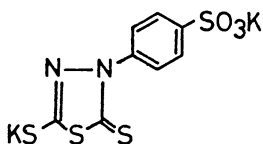


Fig. 6 Bismuthiol-II sulfonate

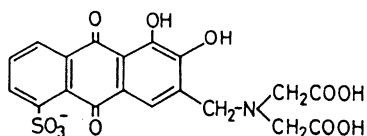


Fig. 7 Lanthanum complex of alizarin complexone sulfonate (ALCS)

On the other hand, we attempted to develop a direct determination method for selenium(IV) and (VI), respectively, by the use of resin loaded with bismuthiol-II sulfonic acid for the elucidation of the oxidation state of selenium in the environment. In an attempt to find suitable reagent which is able to form stable selenotrisulfide from selenium(IV) in the presence of bismuthiol-II sulfonic acid, various reagents including thiols were examined. The addition of thiourea was effective for the collection of selenium(VI) on the resin. On the contrary, various reducing agents were not effective and sometimes the formation of elemental selenium was observed. In the systems of selenium(VI), thiourea and the resin loaded with bismuthiol-II sulfonic acid, it seems likely that selenium(VI) is reduced to a lower oxidation state by thiourea and forms selenotrisulfide first with thiourea, and then with bismuthiol-II sulfonic acid, the latter being more stable. In this reaction, the function of thiourea may not simply be the reduction of selenium(VI). The mechanism of this reaction is now under study. We have established a procedure which is applicable to the environmental water sample for the respective determinations of selenium(IV) and (VI). Selenium(IV) is collected with a column packed with the resin loaded with bismuthiol-II sulfonic acid and selenium(IV) is eluted with penicillamine solution and the eluate is applied to the fluorimetric determination of selenium. The sample solution containing selenium(VI), that is the eluate after selenium(IV) is adsorbed on the resin, is mixed with thiourea solution and applied to the column packed with the resin loaded with bismuthiol-II sulfonic acid. Selenium is converted into selenotrisulfide and adsorbed on the resin, and determined in a similar manner to the case of selenium(IV). This procedure was applied to some environmental water samples and gave reasonable results.

The extremely high stability of penicillamine selenotrisulfide allowed us to develop a novel method for the determination of low levels of selenium. The method is based on HPLC of the fluorophore derived from penicillamine selenotrisulfide and 4-fluoro-7-nitrobenzo-2,1,3-oxadiazole. The limit of determination for selenium(IV) by this method is as low as pmol level, and the procedure is much simpler than in the conventional fluorimetric method. We attempt to establish a system for the analysis of selenium by the combination of this fluorescent detection with the resin loaded with bismuthiol-II sulfonic acid as a selective sorbent.

FUNCTIONAL RESIN FOR SEPARATION AND DETERMINATION OF FLUORIDE ION

A new functional resin for the separation of fluoride ion was prepared by the modification of anion-exchange resin with lanthanum complex of alizarin complexone sulfonate (ALCS) (Fig. 7) (ref. 7). ALCS was synthesized from alizarin-5-sulfonic acid and iminodiacetic acid by Mannich condensation reaction. ALCS-La complex immobilized on the anion-exchange resin by both ion-exchange and physical adsorption forms stable ternary complex with fluoride ion on the resin. Adsorption of fluoride ion by the resin loaded with ALCS-La complex was almost complete and fluoride ion adsorbed was eluted with sodium hydroxide solution effectively, and the resin can be used repeatedly (Fig. 8). The unselective adsorption of fluoride ion as an anion by a simple ion-exchange is also observed to some extent. The presence of common cations and anions interfered the unselective adsorption of fluoride ion, but not the selective adsorption of fluoride ion at lanthanum site. However, aluminum(III) interferes the adsorption of fluoride ion seriously through the formation of extremely stable its fluoride complex. The masking ability of the common chelating agent was insufficient to eliminate the interference caused by aluminum. Deferoxamine (Fig. 9) was found to be an effective masking agent for aluminum. We established a procedure for the preconcentration of fluoride ion by the use of the functional resin as a sorbent and deferoxamine as a masking agent. The procedure is applicable to the determination of fluoride ion of the concentration which is lower than that can be determined by ion selective electrode method. This method is useful for the preconcentration of fluoride ion in environmental and biological samples, instead of the conventional separation method, which is based on the diffusion of hydrogen fluoride.

FUNCTIONAL RESIN FOR DETERMINATION OF HYDROGEN PEROXIDE

We found peroxidase-like and catalase-like activities of anion-exchange resin loaded with some water soluble metal complex of porphyrin. The aqueous solution of some metal complexes of porphyrin accelerates the decomposition of hydrogen peroxide, but it is oxidized irreversibly. On the contrary, some metal complexes of porphyrin immobilized on the ion-exchange resin

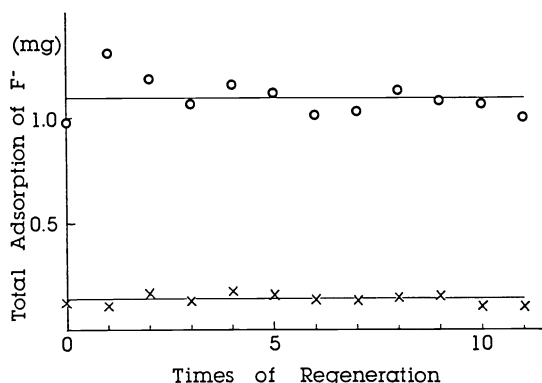


Fig. 8 Reuse of resin loaded with ALCS
(o) resin loaded with ALCS
(x) anion-exchange resin(Amberlite CG400)

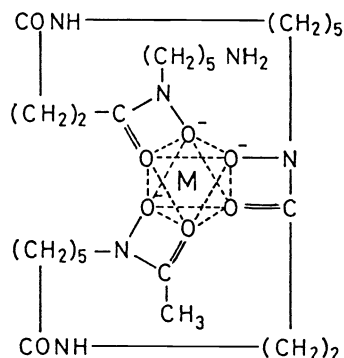
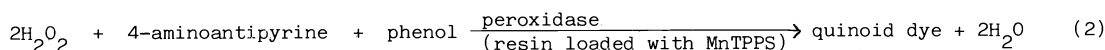


Fig. 9 Possible structure of deferoxamine-metal(III) complex

enhances the decomposition of hydrogen peroxide catalytically and their activity resembles that of peroxidase and catalase. The anion-exchange resin loaded with Mn(III)-tetrakis-(sulfo-phenyl) porphyrin (MnTPPS), which was found to be the highest in the activity among the resins loaded with various metal complexes of porphyrin exhibited the comparable efficiency to that of peroxidase (Fig. 10). The activity was estimated through the formation of the dye formed by a reaction



The optimal pH for this reaction was found to be 7, which is also optimal for the reaction of peroxidase. On the other hand, anion-exchange resin loaded with MnTPPS also exhibited the highest activity which resembles the activity of catalase (Fig. 11). The catalase-like activity was confirmed through the formation of a dye formed from formaldehyde which is produced from methanol by hydrogenperoxide and the resin loaded with MnTPPS. The optimal pH for this reaction was found to be 11, which is also optimal for the reaction of catalase. The catalase-like activity of the resin loaded with MnTPPS reached approximately twice of the activity of catalase. In these functional resins, water soluble metal complex of porphyrins behave as the functional reagent depending upon the presence of sulfonate group which is available for the ion-exchange with anion-exchange resin and strong physical adsorption of the reagent onto the anion-exchange resin and in addition the enzyme-like activity. The activity of these resins does not deteriorate even in the repeated use of many times. New methods of the determination of hydrogen peroxide were established by the use of the anion-exchange resin loaded with MnTPPS instead of

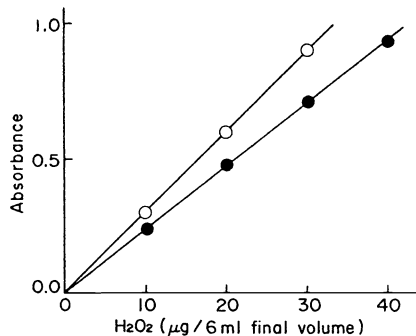


Fig. 10 Calibration graphs for determination of H_2O_2
(●) with the resin loaded with MnTPPS
(o) with peroxidase

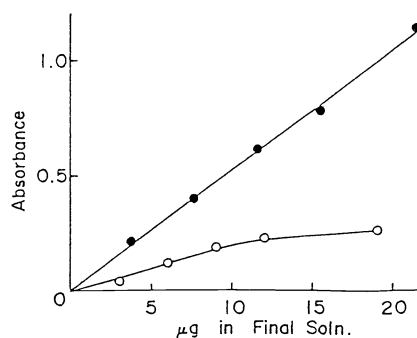


Fig. 11 Calibration graphs for determination of H_2O_2
(●) with the resin loaded with MnTPPS
(o) with catalase

peroxidase (ref. 8) and catalase (ref. 9). These methods are expected to be applied to the routine analysis for clinical purpose. The anion-exchange resin loaded with MnTPPS is regarded as an artificial mimesis of peroxidase and catalase, which have been used widely in analytical chemistry. The use of the artificial mimesis in place of enzyme or immobilized enzyme is advantageous based on its high stability and ease of the preparation. Design of the terfunctional reagent will lead the further development of the functional resins, which are useful in analysis.

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