

Interaction of Orthophosphate with Iron(III) and Aluminum Hydroxides

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■ The influence of pH and aging upon the phosphate binding capacity of iron(III) or aluminum hydroxides has been investigated. The formation of reactive polynuclear hydroxo complexes by the hydrolyzing cations and the subsequent oxolation process are starting points of a discussion of the observed influence of the experimental conditions upon the rate and extent of phosphate adsorption. The ratio between the quantity of phosphate adsorbed and the concomitant release of hydroxyl ions has been measured and interpreted in terms of change in charge of the complexes formed. Some practical consequences of the iron/aluminum interaction with phosphate for water treatment processes such as coagulation, deferrization of groundwater, and for phosphate release from iron-rich sediments are explained in terms of effects of pH, aging, and charge.

Aluminum and iron salts have drawn considerable interest from environmental chemists due to their applications as flocculants in water treatment (1, 2) and as phosphate removing agents in tertiary sewage treatment (3-5). Application of phosphate fertilizers has stimulated soil chemists to investigate the role of oxides of iron and aluminum in the fixation of phosphates (6, 7). More recently, the role of these oxides in the exchange of phosphate between sediments and overlying water has also been recognized (8-12). In many lakes and reservoirs a substantial part of the phosphate binding capacity of the sediments is due to these cations, and hence these elements are major variables in the eutrophication process.

Numerous small-scale and laboratory studies have been performed on phosphate removal from solution by oxides and hydroxides of aluminum and iron under varying conditions of temperature, pH, ionic strength, and phosphate concentration (3, 4, 13-22). A qualitative interpretation of the observed phenomena could be presented in most cases. For some well-defined systems, a model of ion adsorption with considerable predictive capability has been presented (17, 19, 31). In most studies the materials used were more or less crystalline oxides such as α - Al_2O_3 (15, 16), α - Fe_2O_3 or hematite (21, 22), and α - FeOOH or goethite (18, 21), often with a well-defined particle size and (or) specific surface area. Also, the structure of the goethite surface and the conformation of adsorbed phosphates have received much attention (20, 23, 24).

In the research reported here, mainly freshly precipitated amorphous hydroxides have been used. Owing to aging effects, such systems exhibit irreversibility in adsorption behavior and are generally less amenable to quantitative interpretation. The main goal of this study is to contribute to the understanding of the effects of pH and aging upon phosphate adsorption and to discuss some of the implications for phosphate removal processes and for phosphate exchange between sediments and overlying water.

Materials and Methods

Analytical reagent grade chemicals [KH_2PO_4 , $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, HNO_3 , and NaOH], demineralized water, and Pyrex glassware were used. Sartorius membrane filters (SM11306) with a $0.45\text{-}\mu\text{m}$ pore size were used for suspension filtration. A Knick mV-pH meter with Ingold combination electrode was used for pH measurement. Phosphate concentration was determined by the modified Murphy-Riley method (25). Absorbance was measured at 840 nm

on a Zeiss PMQ II spectrophotometer. Aluminum and iron concentrations were determined by atomic adsorption using a Varian Techtron Model 1100 AA meter.

In adsorption experiments known volumes of concentrated phosphate solutions were added dropwise from a microburet to a stirred suspension of iron or aluminum of the same pH. The pH was readjusted at the preset value, and the amount of acid required to maintain the pH was calculated from the strength and volume added, including a correction for the dilution effect. This correction was measured by adding the same volume of phosphate solution to a volume of water corresponding to the iron or aluminum solution and again adjusting the pH. Both freshly precipitated and aged suspensions of the metal hydroxide were used in these experiments.

In other experiments, the sequence of addition was reversed, and a small volume of a concentrated iron or aluminum solution was added dropwise to a stirred, diluted phosphate solution under continuous adjustment of pH.

In all experiments, carbon dioxide was excluded by bubbling with purified nitrogen. The effect of ionic strength has not been investigated. Unless stated otherwise, the contact time applied in the experiments was 24 h, after which samples were withdrawn and filtered. The filtrate was analyzed for its phosphate concentration.

Reversibility of adsorption due to pH change was studied by stepwise changes of the pH of suspensions of iron hydroxy phosphate, allowing equilibration for a fixed time, sampling, and further changes in the pH.

Results

Figure 1 presents adsorption isotherms of phosphate on iron(III) hydroxide, freshly precipitated at the indicated pH, with 15-min contact time. Initial iron concentrations used were of the order of $10^{-4}\text{ mol L}^{-1}$. For aluminum, similar curves are obtained.

The effect of reversal of the reagent addition is shown in Figure 2. All further conditions being the same, the only difference is that the dashed lines represent the adsorption isotherms for phosphate solutions added to freshly precipitated aluminum hydroxide at pH 7 and 8, whereas the solid lines result from addition of concentrated aluminum solutions to dilute phosphate solutions of pH 7 and 8, respectively, such that the hydroxide precipitate is being formed in the presence of phosphate ions.

Another experiment demonstrating the effect of hydroxide age is visualized in Figure 3. Both a fresh and a 1-day-old suspension of iron(III) hydroxide containing about 5 mg of iron/L received 3 mg of $\text{PO}_4\text{-P/L}$. The degree of adsorption was followed in time. The fresh precipitate exhibited the greater binding capacity. Obviously in both systems the sorption equilibrium was not reached within 24 h.

Time-dependent and hysteresis effects are further shown in Figure 4. The phosphate concentration after 1 h or after 1 day of equilibration in the presence of hydroxide at pH 7 is determined. Then, by addition of acid or base, the pH is shifted 2 units, and the suspension is left again 1 h or 1 day before sampling. It can be seen that the adsorption and desorption of phosphate due to pH changes generally are not completely reversible. Information on the mechanism of phosphate adsorption can be obtained by measurement of the amount of OH^- desorbed from the hydroxide upon adsorption

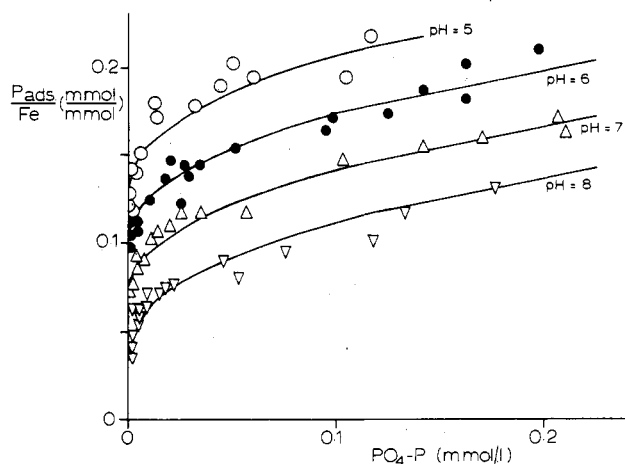


Figure 1. Adsorption isotherm of phosphate on freshly precipitated iron(III) hydroxide

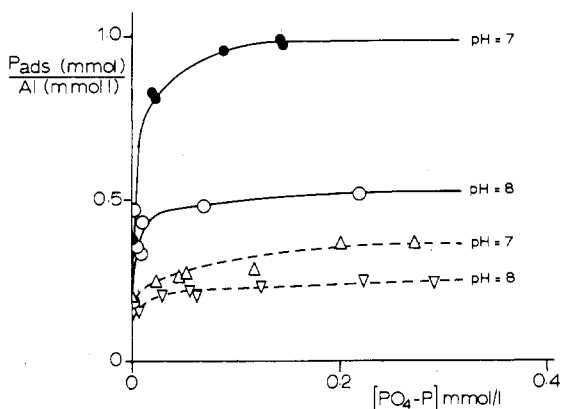


Figure 2. Phosphate adsorption on aluminum hydroxide: (—) aluminum solution added to phosphate solution; (---) phosphate solution added to aluminum precipitate

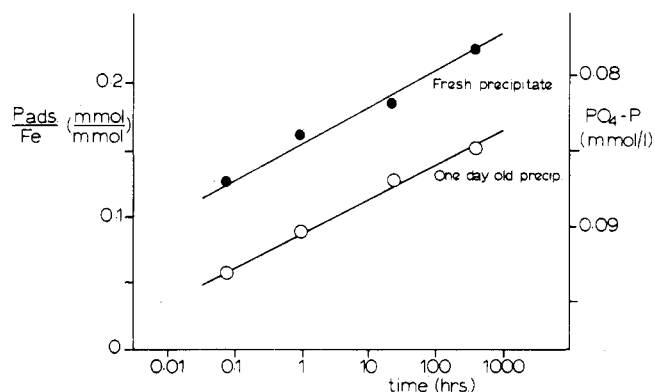


Figure 3. Phosphate adsorption by iron(III) hydroxides as a function of time

of phosphate. The ratio R in moles of OH^- per mole of phosphate adsorbed is determined by measurement of the amount of acid required to keep the pH constant during adsorption of phosphate and correction for the blank.

Figure 5 shows that R is a function of both pH and of the extent of adsorption. The results also depend upon the degree of aging. The results presented in Figure 5 were obtained with freshly formed iron(III) hydroxide suspensions with iron concentrations in the range of $0.5\text{--}5.0\text{ mmol L}^{-1}$ at 20°C after 15-min equilibration with the phosphate solution.

Discussion

The literature contains ample evidence for the formation of iron and aluminum (hydr)oxides in solution through in-

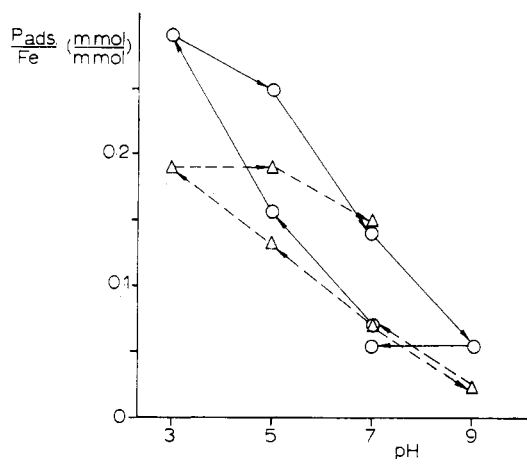
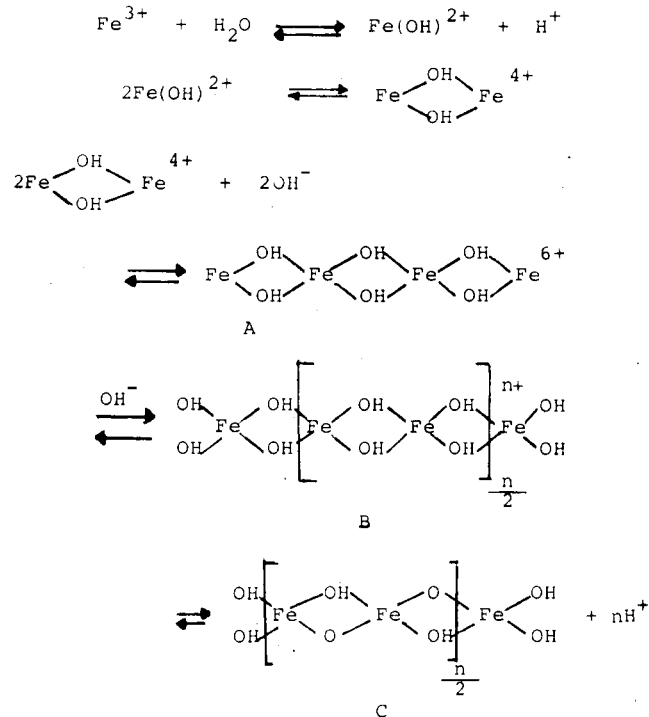


Figure 4. Hysteresis of phosphate adsorption on iron(III) hydroxide as affected by changes in pH; iron concentration, 0.085 mmol L^{-1} ; initial phosphate concentration, 0.096 mmol L^{-1} ; (---) 1-h intervals; (—) 1-day intervals

termediates of monomers and polymers. On the basis of go-stop and go-stop-reverse potentiometric titrations of iron(III) solutions at varying ionic strengths and temperatures, Dousma and de Bruyn (26) derived the following scheme for the hydrolysis-precipitation process:



Structure C represents the large polymers that will form slowly through the so-called oxolation process from polymer B; eventually this may result in goethite ($\alpha\text{-FeOOH}$) and hematite ($\alpha\text{-Fe}_2\text{O}_3$) formation. The oxo bridges once formed react very slowly with acid, whereas monomers, dimers, and polymers of types A and B are formed or decomposed relatively fast. Intermediate structures between B and C involving a variable number of oxo bridges may be visualized. Although not stated explicitly in their paper, the scheme proposed by Dousma and de Bruyn does not necessarily imply a clear distinction between the phases of polymer growth and oxolation.

This scheme is helpful in the explanation of the observed phosphate adsorption phenomena. The extent of polymer formation is decisive for the initial phosphate removal when

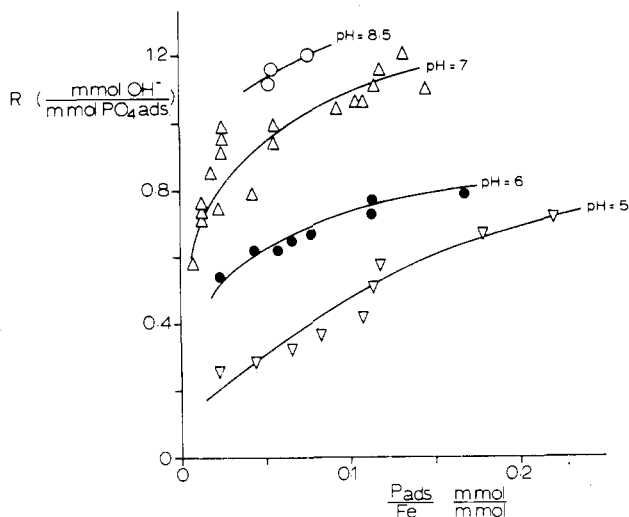


Figure 5. R as a function of pH and extent of adsorption

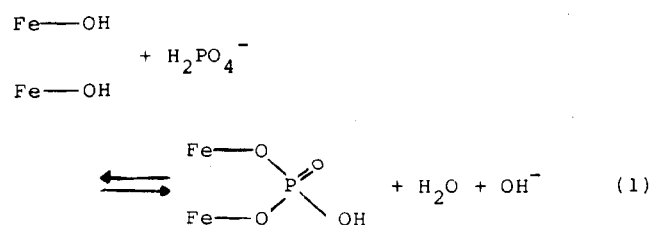
an iron(III) or aluminum solution is mixed with a phosphate solution. The mixing of a concentrated acid aluminum solution with a diluted phosphate solution at pH 7 (Figure 2) under vigorous stirring, while adjusting the pH continuously, results in very effective phosphate binding.

At relatively low phosphate concentration, a complex is being formed with a 1:1 molar ratio of aluminum and phosphate. With a freshly formed hydroxide, the adsorption is less efficient due to the previous formation of polymers resulting in a reduced number of singly coordinated hydroxyl groups. For goethite, evidence for the bridging of two such singly coordinated hydroxyl groups by an adsorbed phosphate ion is available (18, 20, 24, 27). In accordance with these experiments is the observation of Leckie and Stumm that homogeneous precipitation of phosphate by iron(III) formed in situ by oxidation of iron(II) is more effective than precipitation by added iron(III) salts (13). The effect of pH (Figures 1 and 2) can be attributed to the competition of hydroxyl and phosphate ions for iron(III) or aluminum ions.

Further aging of the hydroxide results in a concurrent reduction of the phosphate binding capacity (Figure 3), although a slow process causes the adsorption to increase for both fresh and 1-day-old precipitates.

The same slowly continuing adsorption has been observed for hematite by Breeuwsma (28), although at much higher phosphate concentrations. The time dependency of adsorption and desorption (29) is also demonstrated by the experiments summarized in Figure 4.

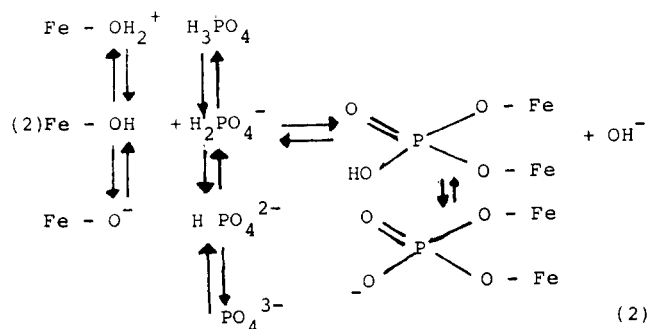
Adjustment of the adsorption equilibrium to a change in pH is a slow process. The slowness of these processes can be attributed to the low rate constant for the exchange of binuclear bound phosphate ions as established experimentally through isotopic exchange measurements with phosphated goethite (18). The slow rearrangement of the phosphate ions on the surface would gradually result in optimal coverage at the prevailing conditions of pH and ionic strength, leaving the minimal number of single coordinated free hydroxyl groups. A simple equilibrium equation (1) represents the effect of pH:



This description assumes a fixed number of single coordinated hydroxyl groups on the surface and does not take into account charge effects.

Especially for the amorphous material used in this research, a shift in equilibria between structures A, B, and C of the polynuclear hydroxide may also contribute to the observed lags in equilibration. Phosphate adsorption will occur primarily at positive sites. The resulting decrease of the surface charge may induce the adsorption of protons and a shift in the general direction from structure C to structure B and a concomitant increase in the number of adsorption sites. The substantial change in the phosphate binding in the experiments of Figure 3 also indicates an increase in the number of adsorption sites.

In terms of Equation 1, this means a refinement allowing a variable number of Fe—OH groups and redistribution of charge through transfer of hydroxyl ions or protons. The latter can be visualized as:



If desired, monodentate forms can be included in this model. For well-defined materials the adsorption isotherms can be described quantitatively with such models (30). For our amorphous material, similar attempts were not completely successful, probably due to the variable number of adsorption sites. However, the adsorption isotherms drawn in Figure 1 fit the equation:

$$\frac{P_{\text{ads}}}{\text{Fe}} = 0.298 - 0.0316\text{pH} + 0.201[\text{PO}_4\text{—P}]^{1/2} \quad (3)$$

with quantities and concentrations expressed in millimoles and millimoles/liter, respectively. Roughly, this equation is in accordance with a view of the adsorption process as a high-affinity adsorption on the positive sites, resulting in approximately complete neutralization of the complex at very low concentrations of phosphate in the solution. The flat part of the isotherm represents the equilibrium of Equation 1 resulting in a dependency of the adsorption roughly proportional to the square root of the phosphate concentration.

The neutralization of the Fe—OH₂⁺ sites would result in a binding of phosphate proportional to ΔpH with respect to the zero point of charge, because the surface charge is controlled by H⁺ ions. Equation 3 therefore would imply a zero point of charge at pH 9.4 in the absence of phosphate. The scatter in the data points is due to the effects of aging.

The equilibration time in the measurement of the adsorption isotherms (Figure 1) was 15 min; the precipitate is still reactive after such a short equilibration time as indicated by pH shifts, and this prevents a good reproducibility of the experiments. However, a major change in the number of adsorption sites as shown in Figure 3 is improbable.

Although this simple description is based on a mixture of arguments, such more or less empirical relations (Equation 3) may be helpful in the modeling of the phosphate-iron interaction in sediments that will be discussed below. Before turning to the practical implications, however, it is useful to discuss briefly the results presented in Figure 5. The adsorption of phosphate results in the release of hydroxyl ions

at all pH values and concentrations studied. Since the pH in the solution is kept constant, the average charge of the adsorbed phosphate ions conforms to the species distribution in solution.

For a pK_2 value of 7.2 for phosphoric acid, this results in a net negative charge for each adsorbed phosphate ion of 1.0, 1.06, 1.39, and 1.98 at pH values of 5, 6, 7, and 8.5, respectively. Although, upon adsorption, hydroxyl ions are released in the quantities shown in Figure 5, the net result of adsorption is a decrease of the charge of the complex. At an adsorption level of 0.07 mmol of P per mmol of iron, the decreases in charge at these pH values are 0.65, 0.41, 0.39, and 0.78, respectively. The more positive the complex was initially, the more effective the neutralization. At pH 8.5 there are probably no positive sites left at this adsorption level, and also the bivalent phosphate ion dominates.

Considering the curves at one pH shows that the R value increases with increasing degree of adsorption. Hence, the increment has a higher R value than the average, which means that positive sites are occupied during adsorption with priority.

Practical Conclusions

The phenomena discussed here are significant in situations where iron or aluminum plays a role in phosphate binding in treatment plants or in the environment. The significance of rapid mixing of the coagulant in water treatment plants for effective destabilization and coagulation of negatively charged particles (e.g., clays) by the positive oligomers parallels the effective phosphate removal (Figure 2). In tertiary treatment of sewage, the phosphate removal efficiency of iron(III) or aluminum salts will depend largely on the fast initial mixing. In several instances also, iron(II) salts are applied, for example, in drinking water reservoirs, to reduce the phosphate level for prevention of excessive algal blooms. Precipitation of the oxidation products formed in situ can be very effective in removing phosphate, but, depending upon dosage, pH, temperature, and phosphate concentration, the iron(III)-hydroxophosphate particles can be restabilized by charge reversal (22, 31). Particularly at low temperatures and in slightly acid waters, the rate of oxidation is low and a very effective adsorption of phosphate can result in negatively charged phosphated complexes resisting coagulation. Also, in the deferrization of groundwaters by aeration and subsequent filtration, a reduction of the removal of iron in the presence of phosphates has been observed (statistics of the Dutch Water Works, 32, 33). This is due to a change in the floc region resulting in incomplete sorption of the colloidal ferric hydroxide by the negatively charged sand particles. The stability regions of hematite in the presence of phosphate as presented by Breeuwsma (22) show a restabilization at phosphate concentrations of $2-3 \times 10^{-5}$ mol L^{-1} for the pH region 7-8.5; at pH 6 a much higher concentration, 3.3×10^{-3} mol L^{-1} , is required. For amorphous material, however, restabilization may occur at lower phosphate concentrations due to the high degree of adsorption. In experiments in which iron(III) (10^{-4} mol L^{-1}) was added to a buffered alkaline phosphate solution (10^{-4} - 4×10^{-4} mol L^{-1}), we observed that subsequent lowering of the pH to a value of 6 was insufficient to obtain a suspension from which all the iron could be removed by membrane filtration with a 0.2- μ m filter. At pH 5 complete removal was achieved.

In the environment, iron often plays a role in binding phosphates in the sediments of lakes and reservoirs. Therefore, the redox and pH conditions control the phosphate exchange processes between sediments and overlying waters. In the oxidized microzone at the surface of the sediment, a variation in pH of the water due to photosynthetic activity can influence the adsorption capacity of the sediment.

More important, however, are the phenomena associated with the annual cycle. In the summer the thickness of the oxidized sediment zone will decrease due to increased organic loading and enhanced bacterial activity induced by higher temperatures. Upon reduction, iron(III)-phosphate-hydroxo complexes present in the sediment will be solubilized as iron(II) and phosphate, the solubility being controlled by the solubility product of vivianite (12) and/or mixed iron(II)-phosphate minerals (8). As a result, iron(II) and phosphate will diffuse simultaneously into the oxidized zone; this process may be enhanced by bioturbation. In the aerobic zone, iron will be oxidized and adsorb phosphate. The local pH and the ratio between the concentrations of iron and phosphate will be of paramount importance in determining the efficiency of this oxidized zone as a lid on the sediment phosphate reservoir. Gradually, the reduced zone will move upward until the whole sediment becomes anaerobic. Now iron(II) and phosphate may diffuse straight into the overlying water.

This water may have a high pH due to carbon dioxide removal by growing algae, whereas the interstitial water in the sediments generally has a much lower pH due to anaerobic or aerobic decomposition of organic material resulting in the production of acids and/or carbon dioxide. Hence, the phosphate binding capacity of the iron(III) hydroxide formed in the water column may be much lower in the overlying water than in the pore water of the sediments and a substantial release of phosphate may occur. Both in shallow lakes and in reservoirs in the Netherlands, where more than 50% of the sediment phosphate was associated with iron, we observed high release rates when both conditions were fulfilled: reducing conditions throughout the sediment and a high pH in the overlying water. The enrichment of the oxidized microzone at the top of the sediment with iron(III) hydroxy phosphate due to diffusion in the period preceding complete reduction can explain the initially very high phosphate flux from sediments upon attainment of the reduced condition before the release rate drops to a fairly constant level (34).

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Gas Chromatographic Determination of Selenium(-II, 0), -(IV), and -(VI) in Natural Waters

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■ Selenium in river water and seawater was determined with electron capture detection (ECD) gas chromatography using 1,2-diamino-3,5-dibromobenzene without preconcentration. The oxidation numbers of selenium are -II, 0, IV, and VI. The reagent can react only with selenium(IV) to form 4,6-dibromopiazselenol, which is extracted into toluene and determined by gas chromatography. After selenium(-II,0) is oxidized by bromine and selenium(VI) is reduced by a bromine-bromide solution to the quadrivalent state, the selenium is determined by the same method, and, thus, the contents of selenium(-II,0), -(IV), and -(VI) are calculated separately. The limit of the determination was 2 ng L⁻¹. Also, the preservation of the sample water is discussed. Selenium(VI) was found to be abundant in seawater.

Chau and Riley (1) maintained that selenium in seawater existed predominantly in the form of selenite ion; meanwhile, Sillén (2) indicated that the selenium was mostly selenate ion. Recently, Sugimura and Suzuki (3) determined the presence of Se(IV) and Se(VI) in seawater in almost equal proportions. On the other hand, Yoshii et al. (4) stated that Se(VI) in natural waters was 1.5-20 times as prevalent as Se(IV).

In a previous paper (5), total selenium and Se(IV), but not Se(-II,0) or Se(VI), in natural waters were determined by ECD gas chromatography. The oxidation numbers of selenium are -II, 0, IV, and VI. This paper will report the individual amounts of Se(-II,0), Se(IV), and Se(VI) in natural waters.

1,2-Diamino-3,5-dibromobenzene can react only with selenium(IV) to form 4,6-dibromopiazselenol, which can be extracted quantitatively into 1 mL of toluene from 500 mL of sample water (5). The selenium(IV) is determined from the peak height of the piazselenol in the gas chromatogram. Selenium(-II,0) is oxidized to Se(IV) quantitatively by bromine solution and selenium(-II,0,IV) is determined by the same procedure. Selenium(-II,0) is calculated from the difference between Se(IV) and Se(-II,0,IV). Selenium(VI) is reduced to Se(IV) by bromine-bromide redox buffer solution, and, at the same time, selenium(-II,0) is oxidized to the quadrivalent state. Thus, the total selenium can be deter-

mined, and Se(VI) is calculated by deducting selenium(-II,0,IV) from the total selenium.

Experimental

Apparatus. A Shimadzu Model GC-5A gas chromatograph, equipped with a ⁶³Ni ECD, was used. A glass column (1 m × 3 mm i.d.) was packed with 15% SE-30 on 60-80 mesh Chromorb W. The column and detector temperatures were maintained at 200 and 280 °C, respectively. The nitrogen flow rate was 28 mL min⁻¹. A Shimadzu Model 101 recorder was used at a chart speed of 5 mm min⁻¹.

Reagents. 1,2-Diamino-3,5-dibromobenzene Monohydrochloride. The synthesis of the reagent was reported elsewhere (5). The reagent (0.6 g) was dissolved in 500 mL of concentrated hydrochloric acid and washed with toluene (25 mL) to remove toluene-soluble matter. The solution was stored in a brown glass bottle and could be used safely for 1 month.

Se(0) Stock Solution (1 mg of Se in 1 mL of CS₂). Elemental selenium (500 mg) was dissolved in 500 mL of carbon disulfide. Working solutions were prepared by appropriate dilution. The concentration of the working solution was determined from the calibration graph by gas chromatography after the conversion of Se(0) to Se(IV) by bromine-bromide redox buffer (6). The solution could be used safely for 1 week.

Se(IV) Stock Solution (0.975 mg of Se mL⁻¹). Selenium dioxide (1.433 g) was dissolved in 1000 mL of distilled water and standardized gravimetrically. The solution was stable for 6 months.

Se(VI) Stock Solution (1.178 mg of Se mL⁻¹). Selenic acid monohydrate (220 mg) was dissolved in 100 mL of distilled water, and working solutions were prepared by appropriate dilution. The concentration was determined by gas chromatography, after Se(VI) was reduced to Se(0) and then oxidized to Se(IV) (6).

Procedure. Pretreatment of Sample Waters. Concentrated hydrochloric acid should be added to the sample water immediately after sampling (1 mL L⁻¹) and filtered by a membrane filter (pore size 0.45 μm) to remove suspended matter as soon as possible.