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Combined Anion-Exchange Separation and Spectrophotometric Determination of Traces of Titanium in Sea Water

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Kombinierte Anionenaustauscher-Trennung und spektralphotometrische Bestimmung von Titanspuren in Meerwasser

Zusammenfassung. Titanspuren wurden in Gegenwart von Thiocyanat durch Anionenaustausch aus der angesäuerten Probe angereichert. Titan wird an Amberlite CG 400 (SCN^-) stark adsorbiert und kann durch Elution mit 2 M HCl – 1,5% H_2O_2 leicht abgelöst werden. Im Eluat wird es spektralphotometrisch mit Diantipyrylmethan bestimmt. Die kombinierte Methode gestattet eine selektive und empfindliche Bestimmung in einer 4 l-Probe von Meer- oder auch Süßwasser. Für einen Gehalt von ~0,4 µg Ti/l beträgt der Variationskoeffizient 7%.

Summary. Traces of titanium in sea water have been preconcentrated by anion-exchange from acidified samples in the presence of thiocyanate. Titanium adsorbs strongly on a column of Amberlite CG 400 (SCN^-) and can be stripped easily by elution with 2 M hydrochloric acid – 1.5% hydrogen peroxide solution. Titanium in the effluent is determined spectrophotometrically with diantipyrylmethane as colour reagent. The combined method allows to determine traces of titanium very selectively and sensitively in sea water as well as non-saline water on a 4 l sample basis. The method yields a coefficient of variation of 7% at a titanium level of ~0.4 µg per l.

Key words: Best. von Titan in Wasser; Ionenaustausch, Spektralphotometrie; Meerwasser.

Introduction

Titanium is widespread in the earth's crust and ranks ninth in abundance. However, scant information is available on the occurrence of titanium in sea water because of lack of sensitive methods of determination as well as effective preconcentration techniques. Contrary to other trace metals in sea water, generally acceptable approaches involving extraction, ion-exchange, cocrystallization, etc. are lacking for this element. Only coprecipitation techniques have been used for the determination of titanium in sea water [2, 8], inconvenient to apply to a large volume of water samples.

Anion-exchange in acid thiocyanate media provides a high capability of collecting traces of metals forming thiocyanatocomplexes from a large volume of water samples. The anion-exchange concentrations in thiocyanate media have been applied to analyses of natural water samples for trace metals involving molybdenum [6, 15], vanadium [9, 16], cobalt [10, 12], silver [7], uranium [13], cadmium, cobalt and uranium [1] and zinc [14], but nothing is known about the capability of this technique for titanium in sea water.

We have reported the strong sorption of titanium on a strongly basic resin from acid thiocyanate media [11]. In this work it will be demonstrated that the thiocyanate concentration system coupled with a sensitive and selective spectrophotometry with diantipyrylmethane [4] provides an quantitative basis for the determination of traces of titanium in sea water as well as non-saline water samples.

Experimental

Reagents and Apparatus. Stock Solution of Titanium(IV). Titanium(IV) tetrachloride of analytical grade was dissolved in 4 M hydrochloric acid to yield 5–10 mg of Ti(IV) per ml solution. This was standardized complexometrically by back-titration with copper(II) sulphate solution using 1-(2-pyridylazo)-2-naphthol as indicator.

Diantipyrylmethane Solution. One gram of diantipyrylmethane was dissolved in 30 ml of 1 M sulphuric acid and diluted to 100 ml with distilled water. Prepared freshly right before use.

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Ion-Exchange Resin. A strongly basic anion-exchange resin Amberlite CG 400, 100 to 200 mesh, in the thiocyanate form was used.

Ion-Exchange Column. Column A. Dried resin (SCN^-) weighing 5.0 g was slurried with distilled water and packed into a column (i.d. 2.5 cm, 10 cm long). The bed was 2.5 cm long. This was used for the purpose of concentration of titanium.

Column B. The dried resin weighing 5.0 g was packed in a conventional column (i.d. 1.5 cm) with distilled water (bed height 6 cm). This was used for the purification of thiocyanate solutions.

Spectrophotometric measurements were made with a Hitachi 101 spectrophotometer in a 5 cm glass cell.

Determination of Distribution Coefficient. The distribution coefficients, *Kd*, for titanium(IV) on Amberlite CG 400 (SCN^-) were measured by a batch equilibrium method. Weighed portions of dried resin (1.0 g each) were placed in glass stoppered conical flasks, to which 41 ml portions of acid – thiocyanate solutions of varying composition were added. The acid thiocyanate solutions were previously adjusted to either 1.0 M or 0.10 M in hydrochloric acid and contained varying amounts of ammonium thiocyanate and 0.106 mmol of titanium(IV). After mechanical shaking for 20 ± 1 h at room temperature, the two phases were separated by filtration. Titanium in the filtrate was determined spectrophotometrically as described below. *Kd* was computed according to:

$$Kd = \frac{\text{amount of titanium in resin phase/g of resin}}{\text{amount of titanium in solution phase/ml of solution}}.$$

Spectrophotometric Determination of Titanium with Diantipyrylmethane. If the sample contains thiocyanate, add nitric acid to the solution and heat gently to destruct the thiocyanate. Cool. Add 1 ml of conc. nitric acid and evaporate to strong fumes. Repeat the nitric acid treatment to complete the decomposition. Dissolve the residue in 2.5 ml of 6 M hydrochloric acid and transfer to a 25 ml volumetric flask. Add 1 ml of 10% ascorbic acid and then 10.0 ml of diantipyrylmethane solution. Dilute to the mark with distilled water. Let it stand for 1 h. Measure the absorbence at 390 nm against the reagent blank.

Ion-Exchange Procedure. Filter the water sample through a membrane filter (0.45 µ Millipore filter). Take a 800 ml portion from the filtrate. Add 91 ml of conc. hydrochloric acid and 20 ml of 30% hydrogen peroxide and reflux for 2 h. Cool. Weigh out 83 g of ammonium thiocyanate, dissolve in 100 ml of distilled water, acidify with 20 ml of 1.0 M hydrochloric acid and dilute to 200 ml with distilled water. Pass the mixture down the column B to remove traces of titanium present in the reagent. Add the thiocyanate effluent to the refluxed water sample above. Load the sample onto the top of the column A at a flow rate of ca. 10 ml per min. Treat additional four 800 ml portions of the Millipore filtered sample (totalling 4 l) in the same way. Wash the column with 250 ml of 1.0 M ammonium thiocyanate – 1.0 M hydrochloric acid solution. Discard the effluent. Strip the titanium by elution with 80 ml of 2.0 M hydrochloric acid – 1.5% hydrogen peroxide solution. Discard the early 30 ml portion of the effluent, collecting the subsequent 50 ml of the effluent. Determine titanium spectrophotometrically with diantipyrylmethane as described above.

Table 1. Distribution coefficients of titanium(IV) on Amberlite CG 400 (SCN^-) in mixed HCl – NH_4SCN media

	NH_4SCN, M					
	5.0	1.0	0.30	0.10	0.030	0.010
1.0 M HCl		$3.3 \cdot 10^3$	$3.4 \cdot 10^2$	40	5.9	< 1
0.10 M HCl	$4.2 \cdot 10^3$	$1.2 \cdot 10^3$	$1.9 \cdot 10^2$	30	< 1	< 1

Table 2. Recovery of titanium from saline water (0.5 M NaCl)

Sample taken, l	Ti added, µg	Ti found, µg	Ti found after correction for blank, µg
4	0.00	0.29, 0.45, 0.20, 0.49, 0.45, av. 0.37	
4	5.10	5.10, 5.49, 5.75, 5.16, 5.69, av. 5.44	av. 5.07 ± 0.30
4	10.2	10.4, 10.5, 10.7, av. 10.5	av. 10.1 ± 0.2

Results and Discussion

The distribution coefficient data on the adsorption of titanium(IV) on Amberlite CG 400 (SCN^-) are tabulated in Table 1 as a function of thiocyanate concentration. Two series of coefficients are obtained, one representing the adsorption from 1 M hydrochloric acid solutions and the other from 0.1 M hydrochloric acid solutions with varying concentration of thiocyanate. Both series of coefficient values increase rapidly with increasing concentration of ammonium thiocyanate. The presence of higher concentration of hydrochloric acid (1.0 M) apparently favours the adsorption of titanium, the coefficient reaching as high as 3.3×10^3 at 1 M thiocyanate concentration. This will be sufficiently high to concentrate traces of titanium on a 5 g resin column from as large as 5 l water samples. The adsorbed titanium thiocyanate complex can be stripped easily by elution with 2 M hydrochloric acid – 1.5% hydrogen peroxide solution. In the ion-exchange procedure given above, 99.0% of titanium can be recovered by elution with this solvent system, while as large as 180 ml is needed to strip 99.4% of titanium adsorbed by elution with 4 M hydrochloric acid. 1 M or 0.5 M sulphuric acid – 1.5% hydrogen peroxide system also allows the quantitative elution of titanium, but takes much more volume of it to complete the elution. Use of perchloric acid appears to be effective, but leads to serious interference with the determination of titanium with diantipyrylmethane.

Based on these observations, we decided to concentrate titanium from sea water sample adjusted to 1 M in hydrochloric acid and 1 M in ammonium thiocyanate, and subsequently to recover with 2 M hydrochloric acid

Table 3. Effect of diverse ions

Foreign ion	Added, µg	Ti, µg		Relative error, %
		Added	Found	
Al(III)	5580	5.10	5.30	3.9
Cd(II)	372		5.05	−1.0
Co(II)	714		5.25	2.9
Cr(III)	2560		8.62	69
	410		5.66	11
	41		5.10	0
Cu(II)	855		5.20	2.0
Fe(III)	1420		5.56	9.0
	708		5.25	2.9
Mo(VI)	202		5.66	11
	101		5.35	4.9
Ni(II)	2700		6.32	24
	270		5.18	1.6
Sb(III)	173		5.15	0.9
U(VI)	268		5.70	12
	134		5.30	3.9
V(IV)	1000		5.30	3.9
V(V)	1000		4.99	−2.2
Zn(II)	1150		5.05	−1.0

Table 4. Determination of titanium in saline water (0.5 M NaCl) in the presence of interfering ions

Run	Sample taken, l	Metal ion added, mg		Ti, µg	
				Added	Found
1	4	Cr(III)	2.05	10.2	10.0, 10.3
2	4	Fe(III)	0.442	10.2	10.1, 10.6
3	4	Fe(III)	22.1[a]	10.2	10.2, 10.7
4	4	Fe(III)	44.2[a]	10.2	10.4, 9.74
5	4	Mo(VI)	10.1	10.2	10.7, 10.4
6	4	Ni(II)	3.38	10.2	10.7, 10.1
7	4	U(VI)	1.34	10.2	10.4, 10.3

[a] Titanium in the effluent determined after separating from Fe(III) by anion-exchange in 6 M HCl

– 1.5% hydrogen peroxide. In this connection we found traces of titanium present in ammonium thiocyanate, which range from 0.9 – 9.1 µg in 415 g portions of ammonium thiocyanate reagents. Purification of the thiocyanate was easily accomplished by passing the reagent solution (adjusted to 0.1 M in hydrochloric acid and 5 M in thiocyanate) down the column B, as described in the procedure. The distribution coefficient of titanium in this condition was as high as 4000, so that we did not find any traces of titanium in the effluent, attaining the goal to get rid of titanium from the thiocyanate reagents.

To apply the anion-exchange thiocyanate system to the concentration of titanium from water samples, artificial sea water (actually 0.5 M sodium chloride solution) spiked with known amounts of titanium was analyzed according to the procedure given, the results being listed in Table 2. On a 4 l sample basis the recoveries are satisfactory for 0, 5 and 10 µg Ti(IV) added, which are at the concentration level of 0.09 ~ 2.5 ppb Ti.

The sorption of thiocyanate complex of titanium and subsequent elution with 2 M hydrochloric acid (1.5% hydrogen peroxide) provide the very selective separation of titanium from a number of metal ions [3, 5, 11] and make it easy to select the colorimetric reagents. Because of its high sensitivity and selectivity we decided to use diantipyrylmethane as the colorimetric reagent for the determination of titanium in the effluent. Results on the interference study with this reagent (see Experimental for analytical conditions) are listed in Table 3, where metal ions are chosen which react with diantipyrylmethane and also are as abundant as or more abundant than titanium in sea water. Assuming even the same behaviour as titanium in anion-exchange concentration and elution steps, the metal ions do not interfere at any significant level with the determination of titanium on a 4 l sea water sample basis.

To confirm the validity of the present method the artificial sea water samples were spiked with Cr(III), Fe(III), Mo(VI), Ni(II) or U(VI) and then analyzed according to the procedure given. The results are shown in Table 4. As a matter of fact, chromium(III) and nickel(II) do not adsorb on the column from the thiocyanate medium, while molybdenum(VI) and uranium(VI) are not stripped from the column by elution with 2 M hydrochloric acid (1.5% hydrogen peroxide). Iron(III) is partially eluted. When iron(III) is present even 32 times as much as the natural sea water level (3.4 ppb), it does not interfere (Run 2). It is necessary to separate the eluted iron(III) when its concentration is as high as 5000 – 10,000 ppb (Runs 3, 4). However, the separation of iron(III) and titanium can easily be achieved by simple anion-exchange in hydrochloric acid media.

Based on these observations, the present anion-exchange-spectrophotometric method appears to provide a sound basis for the determination of titanium in natural waters. The results on repeated determinations of titanium in two sea water and one lake water samples are given in Table 5. In order to have an idea about the accuracy of the method addition tests were also achieved and the overall recoveries were obtained. The recovery and precision (rsd 7 – 9%) are satisfactory.

Before the application of the present anion-exchange-spectrophotometric method to practical water samples, the sample waters were allowed to reflux for 2 h together with hydrochloric acid and hydrogen peroxide to get the possibly ionic solution of titanium,

Table 5. Determination of titanium in natural waters

Sample	Sample taken, l	Anion-exchange method			Coprecipitation method
		Ti, µg		Original Ti content, µg/l	Original Ti content, µg/l
		Added	Found		
Sea water[a]	4	0	1.80	0.450	0.405
	4	0	1.83	0.458	0.388
	4	0	1.65	0.413	
	4	2.55	4.18	0.408	
	4	5.10	7.02	0.480	
				av. 0.442 ± 0.031	av. 0.397 ± 0.015
Sea water[b]	4	0	1.62	0.405	0.350
	4	0	1.53	0.383	0.420
	4	0	1.82	0.455	
	4	2.55	4.28	0.433	
	4	5.10	6.94	0.460	
				av. 0.427 ± 0.033	av. 0.385 ± 0.062
Lake water[c]	4	0	1.69	0.423	0.353
	4	0	1.75	0.438	0.423
	4	0	1.93	0.483	
	4	2.55	4.48	0.483	
	4	5.10	6.65	0.388	
				av. 0.443 ± 0.041	av. 0.388 ± 0.062

[a] Collected at the Kamoike Harbour, Kagoshima Bay, on June 23rd, 1980

[b] Collected on the shore of Yamagawa, Kagoshima Bay, on June 28th, 1980

[c] Collected at the Ikeda Lake, Kagoshima, on June 14th, 1980.

Errors stand for the standard deviation. Values for the coprecipitation method estimated from the range

which may exist in bound or colloidal forms. To confirm further the validity of the whole procedure *another concentration technique involving the coprecipitation of titanium with iron hydroxide* was also examined.

To a 500 ml portion of the Millipore-filtered sample, untreated with the acid-hydrogen peroxide, 22 mg of iron(III) were added, and the iron hydroxide was precipitated with aqueous ammonia. The precipitate was filtered and dissolved in 6 M hydrochloric acid. The hydrochloric acid solution was transferred to the another 500 ml portion of the water, and the precipitation was followed as before. In this way 4 l of the sample was processed. Titanium was then separated from iron(III) by anion-exchange in hydrochloric acid medium and determined spectrophotometrically with diantipyrylmethane as before.

The results obtained are also listed in Table 5. The titanium values thus obtained are scattered, but are in reasonably good agreement with those obtained by the anion-exchange concentration method. The coprecipitation method can be regarded actually as a scavenging technique.

References

1. Gödl, L., Korkisch, J.: Talanta **21**, 1035 (1974)
2. Griel, J. V., Robinson, R. J.: J. Mar. Res. **11**, 173 (1952)
3. Hamaguchi, H., Ishida, K., Kuroda, R.: Anal. Chim. Acta **33**, 91 (1965)
4. Ishii, H.: Bunseki Kagaku **16**, 110 (1967); **21**, 665 (1972)
5. Kawabuchi, K., Hamaguchi, H., Kuroda, R.: J. Chromatogr. **17**, 567 (1965)
6. Kawabuchi, K., Kuroda, R.: Anal. Chim. Acta **46**, 23 (1969)
7. Kawabuchi, K., Riley, J. P.: Anal. Chim. Acta **65**, 271 (1973)
8. Kimura, K., Ikeda, N., Watanabe, H.: Nippon Kagaku Zasshi **73**, 584 (1952)
9. Kiriyama, T., Kuroda, R.: Anal. Chim. Acta **62**, 464 (1972)
10. Kiriyama, T., Kuroda, R.: Fresenius Z. Anal. Chem. **288**, 354 (1977)
11. Kiriyama, T., Kuroda, R.: Anal. Chim. Acta **101**, 207 (1978)
12. Korkisch, J., Dimitriadis, D.: Talanta **20**, 1287 (1973)
13. Korkisch, J., Gödl, L.: Anal. Chim. Acta **71**, 113 (1974)
14. Korkisch, J., Gödl, L., Gross, H.: Talanta **22**, 281 (1975)
15. Korkisch, J., Gödl, L., Gross, H.: Talanta **22**, 669 (1975)
16. Weiss, H. V., Guttman, M. A., Korkisch, J., Steffan, I.: Talanta **24**, 509 (1977)

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