On the Use of Radionuclides in the Study of Behaviour and Physico-chemical State of Trace Elements in Natural Waters

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The applicability of radionuclides for the analysis of the physico-chemical state and behaviour of trace elements in natural waters was studied with six radionuclides in two typical river waters. Adsorption, ion exchange filtration, centrifugation, dialysis and electrophoresis of Ba, Fe, Sc, Zn, Mn and Cr in river water were investigated by a radiotracer method and by instrumental activation analysis. Good correspondence between the results by both methods was obtained only when the radionuclide and corresponding natural element existed predominantly as simple cations at the beginning of experiment. In the other cases, considerable differences in the behaviour of the radiotracer and its stable counterpart were found even after 35 days of equilibration. Very slow isotope exchange was observed particularly with colloidal or organically complexed forms of the natural trace elements. The analysis of the state of trace elements may be further complicated by a change of this state during the time necessary for isotope equilibration. Thus, the radiotracer method has serious limitations in this field.

INTRODUCTION

During the last decade, radionuclides have been extensively used for the study of the behaviour and physico-chemical state of trace elements in natural water systems (see e.g. papers 1–8). Although it has been emphasized in many textbooks of radiochemistry that isotope equilibrium must be established before reliable conclusions can be drawn from the results of

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radiotracer methods, this fact seems to have been often overlooked in investigations related to natural waters. Only a few authors made an attempt to check the extent of isotope exchange that took place in their systems. It has been shown recently that for instance radioactive zinc added to sea water does not exchange with all forms of stable natural zinc even in the course of one year.[9] It seemed interesting to investigate how quickly isotope equilibrium may be established in typical fresh waters. For this purpose, water from two different Norwegian rivers and six radionuclides were chosen to represent at least some points of interest. The behaviour of the added radionuclides and their stable counterparts in the water was compared at intervals after the radiotracer addition. Adsorption on polyethylene containers, retention by cation exchange membrane, centrifugation, dialysis, and electrophoresis were studied simultaneously by radiotracer measurement and instrumental neutron activation analysis.

METHODS

Sampling and labelling

The samples of natural water were collected about 10 cm below the surface of the Glomma River, Fetsund, and the Nitelva River, Lillestrøm, Norway, in February 1974. The original temperature of the water was about 1°C and its pH was 6.9. Altogether 4 liters of each water were taken in two 1-1 polyethylene bottles which had been previously carefully cleaned by dilute solutions of suprapure nitric acid and bidistilled water. Two liters of each water were spiked with radionuclides not later than 1 h after the withdrawal of the water from the rivers.

Six radioactive preparations were used for the present experiments: ^{51}Cr (Na_2CrO_4 in neutral aqueous solution) was obtained from Institutt for Atomenergi, Kjeller. ^{54}Mn, ^{59}Fe and ^{65}Zn in 0.1 M HCl and ^{133}Ba in 1 M HCl were supplied by The Radiochemical Centre, Amersham. A solution of ^{46}Sc was prepared by irradiating solid scandium nitrate in the JEEP-II nuclear reactor (Kjeller, Norway) and dissolving in 0.01 M HNO_3. The approximate specific radioactivities of the preparations are given in Table I. The preparations of ^{54}Mn, ^{59}Fe, ^{65}Zn, and ^{133}Ba were evaporated to dryness and then dissolved in 0.01 M HNO_3. The solutions obtained in this way were mixed in a proper ratio, and then an appropriate amount of ^{46}Sc was added. The mixture was ultrafiltered through Diaflo PM 10 ultrafilter (Amicon N.V., Oosterhout, Holland) to remove possible solid particles present. 0.9 ml of the ultrafiltrate was added to 1l of natural water. Radiochromium underwent no treatment before spiking—0.1 ml of the dilute solution was added to 1l of natural water. The final chemical forms of the

radionuclides and the total concentrations of the corresponding elements added to natural water are presented in Table I, together with the original concentrations of the same elements in the studied waters, as determined by activation analysis. It was found by measurement using glass electrode (GK 2302 C and digital pH-meter PHM 63, Radiometer, Copenhagen) that the pH values of the radioactively labeled and the natural water were the same.

Separation procedures

Both the radioactive and unlabeled waters were analyzed respectively 2 h, 24 h, 7 d and 35 d after the collection. Each analysis consisted of carrying out the separation procedures (centrifugation, dialysis, and ion exchange

TABLE I

Properties of radiotracers and concentrations of the corresponding elements in the studied waters (all concentrations in $\mu g/l$)

Radionuclide	^{46}Sc	^{51}Cr	^{54}Mn	^{59}Fe	^{65}Zn	^{133}Ba
Specific activity (in mCi/mg)	~ 3	360	c.f.*	11.6	380	8.3
Chemical form added	Sc^{3+}	CrO_4^{2-}	Mn^{2+}	Fe^{3+}	Zn^{2+}	Ba^{2+}
Concentration added with radiotracer	5.0	0.1	< 0.4ᵃ	4.5	0.3	1.3
Original concentration in Glomma water	0.082	0.79	19.6	304	10.0	32.1
Original concentration in Nitelva water	0.056	2.1	74.1	474	25.2	19.4

ᵃCarrier-free; determined by activation analysis.

filtration) and preparing two reference samples by pipetting 3 ml of labeled water to polyethylene ampoules or 5 ml of inactive water to quartz ampoules. Several drops of concentrated suprapure nitric acid (Merck A.G., Darmstadt) were added to the ampoules before the sampling to prevent adsorption of trace elements on the walls. Between the samplings the water was allowed to stand undisturbed in closed bottles, but immediately before each sampling the bottle was vigorously shaken to raise particles sedimented.

Centrifugation was done by means of an ordinary laboratory centrifuge (minor type MSE). 10 ml of water were centrifuged in polystyrene tubes for 30 min at about 3000 r.p.m. Subsequently 3 or 5 ml of supernatant were pipetted into polyethylene or quartz ampoules as described above.

For dialysis experiments, a dialysis cell described previously[10] was used. It consisted of two cylindrical compartments made of plexiglass, separated by cellophane membrane cut from Visking tubing (The Scientific Instrument

Centre Ltd., London). 15 ml of water were dialyzed for 24 h at room temperature against the same volume of bidistilled water. Stirring of the solutions was achieved by shaking the cell parallel to the plane of membrane. Samples were taken from the compartment originally filled with bidistilled water.

Ion exchange filtration was carried out by forcing water samples by nitrogen pressure (0.5–1.0 Atp) through Acropor SA–6406 membrane impregnated with strongly acidic cation exchanger (Gelman Instrument Company, Ann Arbor, Michigan). Membranes 25 mm in diameter and a Millipore XX 42 025 10 ultrafiltration cell (Millipore Corporation, Bedford, Massachusetts) were used (new membrane for each water sample to be analysed). The filtered samples were collected directly into polyethylene or quartz ampoules and the filtered volume was determined by weighing.

The free-liquid method by Hoyer et al.,[11] was employed in the study of electromigration. The slightly modified apparatus was made of polyethylene and Tygon (R 3603) tubing. Its central part was filled with the water to be analysed, while both the side parts attached to AgCl-electrode compartments (filled with 0.1 M NH_4Cl) contained ammonium nitrate solution in bidistilled water brought to the same pH value and specific conductivity as the natural water. Then a potential of 260–330 V was applied for 2 h, resulting in a current of 50–100 μA. After the electrophoresis, samples from the central and side parts of the apparatus were taken. The apparatus was then desorbed overnight by suprapure 1 M HNO_3 and samples of the desorption solutions were collected. The specific conductivity of the solutions was measured by conductivity meter CDM 3 (Radiometer, Copenhagen).

Evaluation of results

The samples of the separated fractions and the reference samples were analysed for trace elements by instrumental activation analysis and for radionuclides by gamma spectrometry. The gamma spectra of the solutions in sealed polyethylene ampoules were measured for 10 min by a counting system consisting of two Ge(Li) detectors with associated electronics connected to a small digital computer. Then the ampoules were irradiated for 10 min in the JEEP-II reactor at a thermal neutron flux of about $1.5 \cdot 10^{13} n\,cm^{-2}\,sec^{-1}$ using a pneumatic tube system. After irradiation the samples were transferred from the ampoules into 100 ml screw-cup polyethylene bottles and the gamma peak of ^{56}Mn induced was measured for 10 min. The measurement started exactly 5 min after the end of the irradiation. The inactive samples in quartz ampoules were irradiated batchwise for 4 days at the same neutron flux. Their gamma energy spectra were recorded after two weeks' delay and analyzed for ^{46}Sc, ^{51}Cr, ^{59}Fe, ^{65}Zn and ^{131}Ba. In this case, counting times of 4–10 hours were used.

The quantitative evaluations were based on peak area measurements according to the methods of Sterlinski[12] or Covell.[13] The fractions of each element or radionuclide separated by the filtration and centrifugation or penetrating the dialysis membrane were calculated from the activity of the appropriate sample and that of the corresponding reference sample. Differences in the activities of the reference samples taken from the same bottle after different periods of time served for determinations of relative amounts of the elements lost during the time of storage by adsorption on the walls of the bottle. Electrophoretic mobilities were evaluated as described elsewhere.[14] Total concentrations of elements present in the waters studied were determined from the induced radioactivitity of the first reference samples (taken after 2 h), relative to aqueous standard solutions of the elements in question irradiated simultaneously.

RESULTS AND DISCUSSION

There are two main conditions to be fulfilled for the successful application of a radiotracer method in the study of the state and behaviour of trace elements: 1) the addition of radiotracer must not influence chemical equilibria in the solution; 2) the radionuclide must equilibrate with all the forms of the trace element studied present in the solution.

The first condition is usually fulfilled if the labeling does not significantly increase the concentration of the element studied and does not otherwise change the composition of the solution appreciably. Therefore we added radiotracers in concentrations substantially lower than the original concentrations of the corresponding elements in the water (see Table I) and in solutions of comparatively low acidity in order not to influence the pH. The only exception was scandium, where the addition of radioisotope increased the concentration of scandium by about two orders of magnitude due to insufficiently high specific activity of the [46]Sc preparation available. Possible consequences of this fact are discussed later.

The fulfilment of the second condition cannot be achieved as recommended for other cases by series of chemical treatments (acidification, neutralisation, oxidation and reduction) because of the disturbing effect of these processes on the chemical equilibria in the solution. Instead, the radionuclides should be added in those chemical forms which would be expected to exchange most easily with other possible forms of the respective elements. We chose solutions of cations, except for chromium which was added as chromate. It has been shown previously that a substantial fraction of chromium is present in the waters studied as chromates.[15]

The rivers chosen represent two different types of fresh water. The Glomma

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at Fetsund is a large, rather unpolluted river. The Nitelva is a small river, in Lillestrøm significantly polluted from local industry and dwelling areas. The separation methods used should provide easily reproducible data strongly dependent on the state of the studied radionuclides and elements. Their possibilities and limitations in this respect were discussed earlier.[15]

The results of the adsorption, centrifugation, dialysis and ion exchange filtration experiments are presented in Tables II–VII. They are supplemented by some data on the electrophoretic mobility in Table VIII. Most of the results are average values determined by two independent experiments and four activity measurements. Their error depends both on the separation and evaluation method involved. A somewhat higher precision is observed with the radiotracer method than with activation analysis, because of better counting statistics (higher activity to background ratio) in the radiotracer measurements. As a rough approximation, a standard deviation less than ± 5–7% (absolute) can be assumed for the results of adsorption, ion exchange and centrifugation, with the exception of results close to 0%, which were obtained by comparison of two similar activities, both measured with a certain error. As could be expected, some of these calculations yielded negative results. In such cases, zero is listed instead of the calculated value in Tables II–VII. The reproducibility of the dialysis experiments was about the same for cases of high dialysis (20–50$\%$), but even better for the lower values. Some of the data (those close to 0% for dialysis or 100% for the other methods) are based on calculations involving concentrations or activities lower than the detection limit. In such cases, values "less than" or "more than" are presented in the Tables.

From Table II it follows that radioactive barium added to the waters studied behaves similarly to inactive barium from the beginning of the experiment. No substantial differences were found by any of the methods used. This seems to indicate that isotope equilibrium was established very quickly in this case both in Glomma and Nitelva waters. The most probable form of existence of barium in the waters are simple Ba^{2+} ions, which cannot be sedimented by centrifugation but dialyze rapidly and are retained almost quantitatively by the cation exchanger. The mobility found also corresponds to the mobility of traces of barium ions.[16] Thus the results are in a good correspondence with the well known fact that isotope equilibrium between simple cations is rapidly established.

The isotope exchange of radionuclides ^{59}Fe and ^{46}Sc with natural iron and scandium was very slow and equilibrium was not established even after 35 days. This is proved by the differences in the results of adsorption, centrifugation and ion exchange filtration determined by the activation analysis and radiotracer method respectively (Tables III and IV). The coincidence of dialysis values does not speak against this conclusion, since it merely indicates

TABLE II

Adsorption (ADS), retention by ion exchange filtration (IE), centrifugation (CF) and dialysis (DIA) of trace barium in natural waters (Glomma and Nitelva rivers, Norway) as a function of the time elapsed from the collection of water. The values (given in %) were determined by neutron activation analysis (NAA) or radiotracer method (R)

Method	Time	GLOMMA				NITELVA			
		ADS	IE	CF	DIA	ADS	IE	CF	DIA
NAA	2 h	—	> 95	14	30	—	98	6	28
NAA	24 h	8	95	11	36	7	> 91	8	35
NAA	7 d	6	> 98	3	35	8	> 73	6	—
NAA	35 d	0	> 95	3	35	6	> 88	0	—
R	2 h	—	99	0	29	—	98	1	35
R	24 h	1	99	0	36	4	97	2	42
R	7 d	1	99	8	37	9	98	0	48
R	35 d	0	100	9	40	2	100	0	46

TABLE III

Behaviour of trace iron in natural waters (see Table 2 for explanations)

Method	Time	GLOMMA				NITELVA			
		ADS	IE	CF	DIA	ADS	IE	CF	DIA
NAA	2 h	—	81	56	8	—	87	64	3
NAA	24 h	0	87	56	5	22	90	66	3
NAA	7 d	30	80	70	4	49	84	60	4
NAA	35 d	24	94	83	3	65	78	60	3
R	2 h	—	37	8	2	—	76	19	2
R	24 h	4	61	12	3	6	78	28	1
R	7 d	23	51	30	2	53	80	66	1
R	35 d	42	77	51	5	46	98	96	2

TABLE IV

Behaviour of trace scandium in natural waters (see Table 2 for explanations)

Method	Time	GLOMMA				NITELVA			
		ADS	IE	CF	DIA	ADS	IE	CF	DIA
NAA	2 h	—	81	68	14	—	82	71	< 3
NAA	24 h	15	70	68	3	15	79	71	2
NAA	7 d	32	76	59	3	45	66	61	< 6
NAA	35 d	33	78	63	2	54	83	62	6
R	2 h	—	47	3	1	—	85	29	< 1
R	24 h	5	55	0	< 1	3	79	38	1
R	7 d	11	53	21	1	37	74	47	3
R	35 d	14	47	26	5	54	83	71	3

TABLE V

Behaviour of trace zinc in natural waters (see Table 2 for explanations)

Method	Time	GLOMMA				NITELVA			
		ADS	IE	CF	DIA	ADS	IE	CF	DIA
NAA	2 h	—	80	18	45	—	86	12	42
NAA	24 h	4	80	19	—	5	93	23	36
NAA	7 d	14	81	12	45	12	83	16	40
NAA	35 d	14	81	20	—	4	93	6	—
R	2 h	—	~ 100	1	27	—	96	3	29
R	24 h	0	~ 100	0	30	5	96	3	35
R	7 d	4	~ 100	15	29	7	96	11	39
R	35 d	6	~ 100	13	35	2	~ 100	11	39

TABLE VI

Behaviour of trace manganese in natural waters (see Table 2 for explanations)

Method	Time	GLOMMA				NITELVA			
		ADS	IE	CF	DIA	ADS	IE	CF	DIA
NAA	2 h	—	89	16	32	—	98	5	36
NAA	24 h	16	97	29	28 ·	24	92	2	39
NAA	7 d	42	98	46	23	33	92	84	6
NAA	35 d	44	—	64	25	50	> 94	94	3
R	2 h	—	99	0	31	—	98	0	35
R	24 h	0	99	0	37	3	96	2	42
R	7 d	23	100	57	18	14	99	89	4
R	35 d	32	100	63	29	32	100	95	2

TABLE VII

Behaviour of trace chromium in natural waters (see Table II for explanations)

Method	Time	GLOMMA				NITELVA			
		ADS	IE	CF	DIA	ADS	IE	CF	DIA
NAA	2 h	—	4	29	34	—	56	36	18
NAA	24 h	0	60	41	40	5	54	48	15
NAA	7 d	10	59	50	24	32	39	28	28
NAA	35 d	0	51	35	32	59	28	29	41
R	2 h	—	0	0	45	—	17	4	40
R	24 h	0 ·	8	0	41	4	13	4	40
R	7 d	0	18	8	41	22	13	5	43
R	35 d	27	24	13	13	35	52	51	12

that both the radiotracer and the natural element were present in the colloidal state. It is further supported (according to 17) by the predominantly negative mobility of radioiron and radioscandium (see Table VIII). The prevalence of the colloidal forms of both elements explains the lack of isotope equilibrium, since the isotope exchange between colloids is usually a very slow heterogeneous process, unless rapid recrystallization or redissolution takes place.

The experiments with scandium seem to indicate a further possible complication in radiotracer experiments. It is clear for experiments where radiotracers of low specific activity are used, that even if isotope equilibrium was established, the major effect could be that the natural element would simulate the behaviour of radiotracer added in excess, and not vice versa. Data for all the four methods in Table IV display a good correspondence between the results of radiotracer and neutron activation experiments with scandium in Nitelva water after 35 days of equilibration. As further seen from Table IV, the behaviour of inactive scandium does not change substantially with time. Consequently, the coincidence can hardly be explained by isotope exchange, which would change the state of natural scandium in water, but more probably by similar properties of radioactive and inactive colloids of scandium. This similarity may be a confusing factor in radiotracer experiments, because it is randomly encountered and need not be easily distinguished from the true isotope equilibrium. It can probably explain also the single coincidences found in the behaviour of natural iron and radioiron (see Table III).

According to the results presented in Table V, the prevailing form of stable zinc in the waters studied was Zn^{2+} ions. Besides that, at least one other form was present, which was little adsorbed on cation exchanger and/or could be centrifuged out. The abundance of this form seems to be a little higher in Glomma than in Nitelva water. Radioactive zinc added to both the waters obviously remains in the form of Zn^{2+} ions. No significant exchange could be observed with the second form of stable zinc, as clearly demonstrated by the almost complete retention of radioactive zinc by ion exchange filtration. It is further supported by the different mobility of stable and radioactive zinc towards the anode (Table VIII).

As indicated in the Introduction, the same kind of incomplete isotope exchange was observed by Piro et al.,[9] for zinc in sea water and interpreted as being due to the presence of complexed forms of stable zinc. The negative mobility of zinc in our case points to an electronegative character of the discussed species. Very probably, some strong organic complexes are present.[15] The proportion of the complexed forms in the fresh waters studied was lower than that reported for sea water.[9] The lower the proportion is, the higher is the isotope exchange and thus the better the analysis of the state of natural zinc by radiotracer method. It may be seen that in the water from

Nitelva the behaviours of stable and radioactive zinc are quite similar after 35 days of equilibration.

The results presented in Table VI display certain differences between the behaviour of manganese in the water of the Glomma and Nitelva rivers stored for at least several days. Nevertheless, in both the cases the storage results in a change of the state of manganese. The change is reflected also by the electrophoretic data (Table VIII). Possible reasons of this change were discussed earlier.[15] Radiomanganese added to both the waters behaves very similarly to natural manganese. This is seen from the fairly good

TABLE VIII

Electrophoretic mobility of trace elements (in 10^{-4} cm^{2}sec^{-1}V^{-1}) in Nitelva water in dependence on the time elapsed from the collection of water and on the method of analysis

Element	Method	Time (d)	Mobility towards cathode	anode
Ba	activation	1	~ 5.6	< 0.2
Ba	radiotracer	1	4.9	0.06
Ba	radiotracer	7	4.9	0.03
Sc	activation	1	0.17	1.5
Sc	radiotracer	1	0	2.1
Sc	radiotracer	7	0	2.0
Mn	radiotracer	1	4.2	0
Mn	radiotracer	7	0.5	0.26
Fe	radiotracer	1	0.03	1.9
Fe	radiotracer	7	0.22	1.2
Cr	radiotracer	1	0.01	5.4
Cr	radiotracer	7	0.07	4.1
Zn	activation	1	2.2	0.83
Zn	radiotracer	1	3.3	0.07
Zn	radiotracer	7	3.3	0.07

coincidence of the results, except in the case of adsorption. This coincidence is probably due to rapid exchange of radiomanganese with cationic forms of stable manganese, which most probably prevailed in the freshly sampled natural water. Once the isotope equilibrium is established, the radioactive tracer appears to represent well the behaviour of the manganese present. Significant differences between the results of activation and radiotracer analysis were found only for centrifugation of manganese from samples of Glomma water stored for a short time, where the equilibrium had not yet been established. A further difference can be seen in adsorption results.

The lower adsorption found by the radiotracer method could reflect the fact that part of the stable manganese was adsorbed before the isotope equilibrium has been established, and the isotope exchange between the adsorbed species and the solution is slow.

Table VII contains the data on the behaviour of stable and radioactive chromium. The considerable differences found prove that the isotope equilibrium has not nearly been reached in this case. The most probable reason is slow exchange between the added radiochromate and trivalent stable chromium present in natural water besides the chromates. The trivalent chromium is precipitated or adsorbed on foreign colloidal particles (see the centrifugation results) and therefore the exchange is a slow heterogeneous process. The course of the exchange may be seen from the increase in the retention of radiochromium during dialysis and ion exchange filtration, and from the increase of adsorption and centrifugation. It is further indicated by the decrease in the electrophoretic mobility of radiochromium to the anode (Table VIII). It cannot be excluded, however, that the changes were due to reduction of hexavalent radiochromium to the trivalent state by organic impurities in water. The quantitative analysis would also be complicated by the spontaneous changes of the state of stable chromium in the waters studied, as evident from Table VII. Thus it can hardly be assumed that radiochromium added to natural water would reflect the original state of stable chromium in any reliable way.

CONCLUSIONS

It follows from the above discussion that only one of the six radionuclides studied (^{133}Ba) easily equilibrated with its stable counterpart in natural water. Fairly good coincidence, was also found between the behaviour of radiomanganese and stable manganese, but the state of this element in natural water changed during the equilibration, so that the results of the radiotracer method did not characterize the original state of manganese. Radiozinc approximately equilibrated with inactive zinc only after 35 days in Nitelva water. In the other cases the added radionuclides behaved differently from the corresponding stable elements and therefore could not represent the behaviour and state of the natural trace elements. Furthermore, the behaviour and state of trace iron and chromium changed during the time necessary for isotope equilibration. It can therefore be concluded that a radiotracer method has serious limitations in this field and its results must be considered very carefully before definite conclusions about the physicochemical state and reactions of trace elements in natural waters can be drawn.

Acknowledgements

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