DETERMINATION OF TRACE AMOUNTS OF COBALT BY HOMOGENEOUS ISOTOPE EXCHANGE IN AN ORGANIC PHASE

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A new radiochemical method for determining trace amounts of cobalt has been worked out. It is based on a homogeneous isotope exchange between cobalt(III) diethyldithiocarbamate and cobalt(III) caprate in an organic phase. The method, tested in the range 0·005—8 µg Co, has proved to be selective.

The methods based on isotope exchange[1] consist, in general, in adding a standard quantity of a compound MB, containing a known amount (m) of element M, to an unknown amount (x) of this element in a compound MA. If one of the compounds is labelled with a radioactive isotope of element M of activity A_0, then, after an isotope equilibrium has established, the specific activities of element M in the two compounds are the same; it applies that

$$\frac{A_0 - A_{MA}}{m} = \frac{A_{MB}}{m} = \frac{A_{MA}}{x}, \qquad (1)$$

where A_{MA} and A_{MB} denote the activities of the respective compounds. After separation of the two compounds and measurement of their activities the unknown amount, x, of element M in the sample can be calculated from equation (1) or read from a calibration line. In the latter case it is not necessary to know exactly the added amount (m) of element M in the compound MB. Prerequisites of the method are a sufficiently fast isotope exchange and the possibility of a quantitative separation of the two compounds.

An example of this procedure is the determination based on homogeneous isotope exchange of a metal M between two complexes, M_{AN} and M_{BN}, dissolved in an organic solvent immiscible with water. After an isotope equilibrium has established, one of the complexes is taken into an aqueous phase; a quantitative separation is achieved if the extraction constants of the two complexes are sufficiently different. The isotope exchange of metals between diethyldithiocarbamates and iodide complexes in carbon tetrachloride or a mixture of carbon tetrachloride and amyl acetate was employed to determine Bi (ref.[1]), As (ref.[2]) and Sb (ref.[3]).

The present paper describes determination of trace amounts of cobalt by a procedure based on this principle.

EXPERIMENTAL

Activities of the samples in glass ampoules were measured by a NaI(Tl) well-type crystal connected to a spectrometric apparatus. All the chemicals were of A.G. purity, chloroform was

further purified by distillation. Twice distilled water was used for preparation of the solutions. The stock solution of cobalt(III) caprate was prepared as follows: 0·344 g of capric acid was dissolved in c. 200 ml of water, neutralised with 3·4 ml of 2·6% NH$_3$ and diluted with 400 ml of water (I). 0·290 g of CoCl$_2$.6 H$_2$O was dissolved in 100 ml of water and 5 ml of 30% H$_2$O$_2$ was added to the solution. After 30 minutes' standing with an occasional stirring the excess of the peroxide was removed by boiling (II). The solutions I and II were combined and the precipitated cobalt(III) caprate was collected on a filter, washed with water and acetone and dried in a vacuum evaporator at 30°C. An adequate amount of the precipitate was dissolved in chloroform and the concentration of cobalt was adjusted to about 3 μg/ml. This solution was stable for 5 days at least. Prior to use it was diluted with chloroform in a ratio of 1 : 10 to 1 : 100. Since the oxidation was not quantitative, or as a result of the subsequent reduction to remove the excess of the oxidant, the solution was a mixture of cobalt(II) and cobalt(III) caprates. The cobaltous salt does not, up to a certain concentration, interfere with the determination and neither does free capric acid, if present. The exact concentration of Co(III) in the precipitate need not be known but can be determined by the method. A solution of Co(II) chloride containing radionuclide ^{60}Co, with a negligible amount of the support, was used for the labelling.

RESULTS AND DISCUSSION

Cobalt(II) can be quantitatively extracted into chloroform in the form of Co(III) diethyldithiocarbamate[4] from an aqueous medium in a pH range of 2 to 12 (the oxidation of Co(II) diethyldithiocarbamate to the Co(III) salt is spontaneous). Preliminary experiments showed that in the extraction of Co(II) from a solution of 1M-NaOH and 0·1M sodium diethyldithiocarbamate the separation is also quantitative
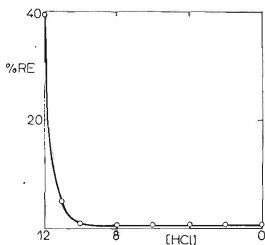

FIG. 1

Percentage of Re-extraction (% RE) of Cobalt(III) Diethyldithiocarbamate in Relation to Concentration of HCl

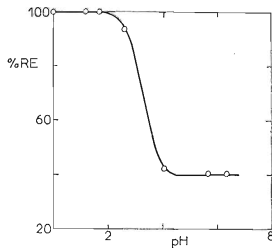Time of shaking 3 min, phase volume 5—10 ml.

FIG. 2

Percentage of Re-extraction (% RE) of Co in the Form of Caprate in Relation to pH of the Aqueous Phase

Time of shaking 30 s, phase volume 5—10 ml.

after 3 minutes' shaking. The extraction from this medium is more selective, the excess of the chelating agent remains quantitatively in the aqueous phase[5].

We studied the transfer of cobalt (labelled with ^{60}Co), in the form of Co(III) diethyldithiocarbamate, from chloroform into hydrochloric acid in relation to concentration of the latter (Fig. 1). Re-extraction of cobalt in the form of caprate in chloroform into mixtures of hydrochloric acid and ammonium chloride of different pH values was studied analogously (Fig. 2). The two Figs show that optimum separation of the two compounds can be obtained by 30 seconds' re-extraction of Co(III) caprate into 2 to 8M-HCl.
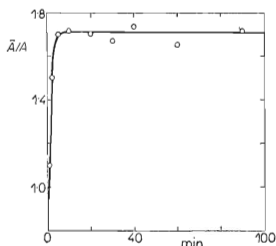

FIG. 3

Exchange Degree, Expressed as Ratio of Activities of the Two Separated Forms of Co(III), $\overline{A}/A$, in Relation to Time t
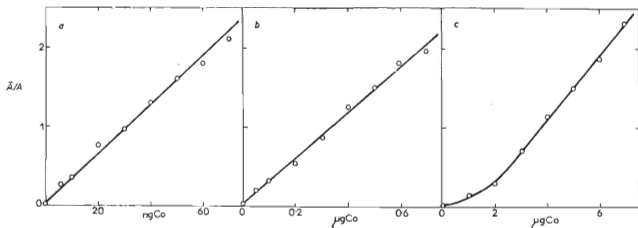

FIG. 4

Ratio of Activities of the Organic and the Aqueous Phases, $\overline{A}/A$, in Relation to the Content of Co in a Sample

To an extract of Co(III) diethyldithiocarbamate was added a) 0·031, b) 0·31, c) 3·1 μg of Co(III) in the form of caprate.

The kinetics and reproducibility of the isotope exchange of Co(III), proceeding between the caprate and the diethyldithiocarbamate in chloroform, were studied radiometrically after labelling the cobalt in the first or the second complex by the radionuclide ^{60}Co. Chloroform solutions of the two forms of Co(III) were mixed and after a time the cobalt in the caprate was re-extracted into 4M-HCl. The activities of equal aliquot portions of the organic and the aqueous phases were measured. The dependence of their ratio on the time of exchange (Fig. 3) shows that the equilibrium was reached in times shorter than 10 min even at the lowest concentration of 0·010 μg CO(III)/ml CHCl$_3$ in the two compounds. Reproducibility of the degree of exchange in the equilibrious state proved to be satisfactory. On the basis of the preliminary experiments described above the following procedure is recommended:

To 5 ml of a neutral solution of Co(II), containing 0·05−0·7 μg Co labelled with ^{60}Co, were added 3 ml of 2M-NaOH, c. 0·5 ml of 1M-sodium diethyldithiocarbamate in 1M-NaOH and 5 ml of CHCl$_3$. After 3 minutes' extraction the organic layer was separated and dried by filtration through glass wool. To 3 ml of this solution was added 1 ml of the ten times diluted solution of cobalt(III) caprate and the mixture was left standing for 15 min. The organic phase was then extracted with 4 ml of 4M-HCl for 30 seconds. The activities of equal aliquot portions of the aqueous and the organic phases were measured. The ratio of activities of the organic and the aqueous phases in relation to the content of Co(II) in the sample is given in Fig. 4. The same dependence at different additions of Co(III) caprate to the extract of Co(III) diethyldithiocarbamate is shown in Fig. 5.

The possible interference by a large excess of other elements with the determination of cobalt by the method described was investigated by the addition of 1 to 100-fold excess of various elements to samples containing 0·5 μg of Co labelled with ^{60}Co of a known activity. The content of cobalt was determined by the method described and the yield of extraction from 1M-NaOH was also ascertained (Table I).

Fig. 5

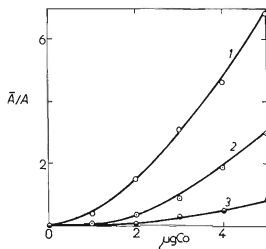Ratio of Activities of the Organic and the Aqueous Phases, $\overline{A}/A$, in Relation to the Content of Co in the Sample at Different Additions of Co(III) Caprate to the Extract of Co(III) Diethyldithiocarbamate

Co(III), μg: *1* 1, *2* 2, *3* 4.

The graphs in Fig. 4 and 5 demonstrate that the method is analytically useful; in the range $0.005 - 0.7$ µg of Co the graphs were linear and obeyed equation (*1*).

If the cobalt to be determined is labelled in the sample and the yield of extraction is known the result is not affected by possible loses due to the manual work or an incomplete separation. With samples containing higher concentrations of cobalt

TABLE I

Determination of Cobalt (0.5 µg) in the Presence of 50 µg of Another Metal

Metal	Yield of Co from the sample %	Found amount µg	Deviation %
Mg(II) Ca(II) Sr(II) Ba(II)	99	0·504	+ 1
La(III) Al(III) Cr(III)	99	0·494	+ 1
Cr(VI) Mo(VI) W(VI) U(VI)	99	0·511	+ 2
As(III) Sb(III)	99	0·505	+ 1
Fe(II)	41	2·86	+ 470
Mn(II)	54	0·612	+ 22
Fe(III)	27	2·23	+ 347
Se(IV)	99	0·85	+ 70
Sn(II)	72	0·455	− 9
Sn(IV)	64	0·53	+ 6
Ag(I)	99	5·04	+ 908
Bi(III)	98	3·44	+ 588
Cd(II)	99	3·55	+ 610
Cu(II)	100	6·58	+1 250
Pb(II)	99	1·07	+ 114
Au(III)	78	1·88	+ 276
Ni(II)	64	9·1	+1 720
	99[a]	0·527	+ 6
	99[b]	0·522	+ 4
Zn(II)	98	0·560	+ 12
	99[a]	0·527	+ 6
	99[b]	0·522	+ 4
Tl(I)	99	4·17	+ 734
	98[a]	2·97	+ 493
	99[b]	0·486	− 3
Tl(III)	99	6·56	+1 210
Hg(II)	98	3·01	+ 503

Another metal: [a] 10 µg; [b] 0·5 µg.

the determination deviated from linearity. A possible cause was an adverse effect of the higher concentration of cobalt(II) caprate.

Selectivity of the method is restricted, since most metals forming diethyldithio-carbamates interfere with the determination, even though they are not extracted from the given medium[4]. Exceptions are U(VI), Mo(VI), As(III), Sb(III), Sn(II) and Sn(IV); Zn(II) and Mn(II) interfere partially. The presence of Fe(II), Fe(III), Sn(II), Sn(IV), Au(III) and Ni(II) decrease the recovery (yield) of cobalt from the solution. They are red — ox elements, Ni(II) is nearly related to cobalt. An opposite effect was always observed in the presence of Cu(II).

The method described was used to determine trace amounts of cobalt in food-stuffs[6].

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