Determination of Total Carbonate by Ligand Exchange*

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An indirect spectrophotometric method is described for the determination of carbonate, based on the decoloration of dilute chloroform solutions of uranium(VI) - *N*-phenylbenzohydroxamic acid by shaking them with an aqueous solution of anions. Several variables affecting the decoloration (pH, shaking time, etc.) were investigated. The carbonate concentration range over which the decoloration of the chloroform solutions showed a linear dependence (30–100 μg ml^{-1} of carbonate in the aqueous phase) and the interferences caused by other ions were also studied. The proposed method was applied to the determination of carbonate in mineral and sea waters and pharmaceutical samples and the results obtained showed good agreement with those obtained using the back-titration method of Gripenberg.

Keywords: *Carbonate determination; spectrophotometry; re-extraction; uranyl chelate; N-phenylbenzohydroxamic acid reagent*

The technique of re-extraction was first applied to the determination of anions in 1975 by Roman and co-workers,[1–4] who investigated the exchange of Fe^{III} [*e.g.*, as iron(III) indole-2-carboxylate into isoamyl alcohol] by using different metal ions, in order to establish methods for the determination of iron. A positive result was only obtained by using Mo^{VI}, although this species is an anion under the experimental conditions. By following this reaction, these workers studied other anions, such as F^-, SO_3^{2-} and CN^- and applied the reaction to the spectrophotometric determination of oxalate[1] and citrate.[2] Similarly, the method was employed to determine cyanide[3] and sulphide[4] by using solutions of copper(II) quinolin-8-olate in chloroform.

This method has been termed "re-extraction via ligand exchange." It is based on the decoloration of dilute organic solutions of metal complexes by shaking them with aqueous solutions of anions. Roman and co-workers[1–4] carried out a theoretical study of this technique and described the ligand exchange reaction. The kinetics of the re-extraction with anions was studied by Haraguchi and co-workers[5–7] using anions such as ethylenediaminetetraacetate (EDTA) and *trans*-1,2-diaminocyclohexane-*N,N,N',N'*-tetraacetate (CyDTA), which react with different metal quinolin-8-olates.

Very few reports have appeared describing the spectrophotometric determination of carbonate.[8–10] In this work, the technique of re-extraction via ligand exchange was applied to the spectrophotometric determination of total carbonate using a solution of the uranyl - *N*-phenylbenzohydroxamate (UO_2 - PBH) chelate in chloroform; the method is similar to that described previously using solutions of uranyl quinolin-8-olate in chloroform.[11] The proposed method was applied to the determination of trace amounts of carbonate in different samples and the results compared favourably with those given by the back-titration method of Gripenberg.[12] The original method of Gripenberg[13] was modified slightly by replacing the indicator with Bromothymol Blue.[14] The amount of carbonate can be calculated from the total alkalinity value and this can be determined by back-titration. Although the apparatus required for this method is simple and the precision is ±0.2%, the analysis takes a considerable amount of time (*ca.* 10 min).

Experimental

Apparatus

Perkin-Elmer Coleman 575 and Shimadzu 120-02 spectrophotometers, equipped with 1.0-cm glass cells, were used for recording spectra or for digital measurements at a fixed wavelength in the visible region of the spectrum.

Metrohm Herisau 620 and Metrohm 645 digital pH meters were used for pH measurements; a Selecta 242 agitator was also employed.

Reagents

As in the Gripenberg method, all solutions were prepared using CO_2-free distilled, de-ionised water; the sodium hydroxide solution was stored protected by an Ascarite tube.

Uranyl - PBH chelate, solution in chloroform. Dissolve *N*-phenylbenzohydroxamic acid (PBH) (0.53% m/v) and uranyl acetate dihydrate (0.068% m/v) in chloroform (mole ratio of ligand to metal, 15.7 : 1), using an agitator over a period of 2 h. This solution is stable for at least 24 h and has an absorption maximum at 510 nm.

Ammonia buffer solutions (pH 7–11). Prepared by conventional methods,[15] by dissolving the appropriate amounts of ammonium chloride and ammonia solution in CO_2-free distilled, de-ionised water. All the buffers had a total concentration of ammonia of 0.5 M.

Carbonate standard solution, 1.000 g l^{-1}. Dissolve anhydrous sodium carbonate (analytical-reagent grade) in CO_2-free distilled, de-ionised water. Dilute the standard solution as appropriate to prepare working solutions daily.

All other reagents and solvents were of analytical-reagent grade.

Procedure

An aqueous solution, containing 20 ml of ammonia buffer solution (pH 8), 20 ml of 2 M sodium chloride and an aliquot of a solution containing 3–10 mg of carbonate were placed in a 250-ml separating funnel and the total volume was adjusted to 100 ml with distilled water. This solution was shaken with 10.0 ml of a solution of the UO_2 - PBH chelate in chloroform for 2 min. The two phases were separated and the organic phase was dried using anhydrous sodium sulphate. The absorbance at 510 nm was measured against a blank prepared in the same way but without carbonate. Calibration graphs were obtained using known amounts of carbonate treated in the same manner.

It should be noted that most of the carbonate is present as hydrogen carbonate at pH 8.0; therefore, the anion that interacts with the UO_2 - PBH chelate is HCO_3^-. However, it is possible to apply the method to any carbonate species, albeit via the HCO_3^- anion. Hence the method determines total carbonate.

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Results and Discussion

Properties of Chloroform Solutions of the UO_2 - PBH Chelate

There are some features of the organic solution that must be known before it can be used for the re-extraction reactions. These include the absorption spectrum and the stability of the organic solution of the metal complex and the pH range in which the metal complex remains in the organic phase after re-extraction with the aqueous phase containing no analyte.

The absorption spectrum of a solution of the metal chelate in chloroform was the same as that reported previously[16] for the liquid - liquid extraction of uranium with solutions of PBH in chloroform (metal: ligand stoicheiometry, 1 : 2).

The stability of this solution was determined by measuring the absorbance (at 510 nm) at various time intervals. The results obtained showed that dilute solutions (1.6×10^{-3} M) of the UO_2 - PBH chelate are stable for at least 24 h. Similarly, the influence of the elapsed time between the preparation of the organic solution and the re-extraction procedure, *viz.*, the ageing of the metal chelate solution, was studied. The results obtained by following the procedure were satisfactory because the decoloration values obtained were reproducible over a period of 24 h.

In order to establish the pH range in which the complex remains in the organic phase, a solution of the metal complex (1.6×10^{-3} M) was prepared and shaken with aqueous phases of different pH values (obtained by adding dilute hydrochloric acid or sodium hydroxide solution) in 250-ml separating funnels. The results showed that a pH of between 7 and 10 was adequate for the re-extraction of the chelate, particularly when NaCl (0.2 M) was added to the aqueous phase (Fig. 1).

Spectrophotometric Determination of Total Carbonate Using Organic Solutions of the UO_2 - PBH Chelate

Effect of pH on the re-extraction

Different samples were prepared in several 250-ml separating funnels by shaking 10.0 ml of the organic solution with 100 ml of an aqueous solution containing different buffers [H_3BO_3 - NaOH, 0.05 M; H_3BO_3 - H_3PO_4 - CH_3COOH - NaOH, 0.05 M (universal buffer); and NH_4Cl - NH_3, 0.1–0.45 M] of various pH values (7–10) and 10 mg of carbonate.

The decoloration obtained using the borate buffer restricted the pH range for the re-extraction to pH values near to neutral (pH 7.5), making the optimum pH range very narrow. When the universal buffer was used a precipitate formed in the organic phase. The results obtained with the ammonia buffer were better. Hence, the decolorations obtained resulted in a high sensitivity for the re-extraction and an increase in the optimum pH range, particularly when the buffer concentration in the aqueous phase was increased (from 0.1 to 0.45 M). However, the optimum pH range was shifted to values near to neutral, where the buffer capacity was smaller. In spite of this, similar results obtained with a buffer of concentration 0.45 M were obtained with an aqueous phase containing a buffer concentration of 0.1 M and 0.4 M NaCl.

Influence of the shaking time of the two phases and the mole ratio of ligand to metal in the organic phase

By following the steps outlined under Procedure, different samples were prepared by varying the mole ratio of PBH : UO_2 added to the organic solution employed. At the same time, the shaking time was also varied. The aqueous phase contained 10 mg of total carbonate in all instances.

The results obtained (Fig. 2) show that the decoloration produced by carbonate ($A_I - A_{II}$, where A_I is the absorbance of the re-extract with no carbonate in the aqueous phase and A_{II} is the absorbance of the re-extract with 100 μg ml^{-1} of carbonate added to the aqueous phase) is similar when the mole ratio of ligand to metal is 15.7 : 1. The absorbance measurements show good reproducibility; a shaking time of 2 min was found to be suitable for re-extraction with carbonate. As can be seen from Fig. 2, it is necessary for an 8-fold excess of ligand to be present in the organic phase otherwise the metal chelate is re-extracted by the aqueous medium containing no carbonate. On the other hand, a 16-fold excess of PBH over UO_2 is inadequate as the metal chelate is not re-extracted by carbonate.

Calibration graph

Beer's law is obeyed, *viz.*, the decoloration of chloroform solutions of the UO_2 - PBH chelate shows a linear dependence over a range of total carbonate concentrations of 30–100 μg ml^{-1} in the aqueous phase. By following the steps outlined under Procedure, decoloration values were obtained for absorbance measurements of the organic samples at 510 nm.

The least-squares equation describing the calibration graph is $A = 0.0054c - 0.0836$, where c is the total carbonate concentration in the aqueous phase in μg ml^{-1} and A is the decoloration value.

The correlation coefficient obtained is 0.999. The sensitivity of the determination, expressed in terms of the apparent molar absorptivity at 510 nm, was 0.324×10^3 l mol^{-1} cm^{-1}. The method can be applied to carbonate concentrations below 30 μg ml^{-1}, but in this instance it is necessary to construct a working curve and/or to employ the method of standard additions.

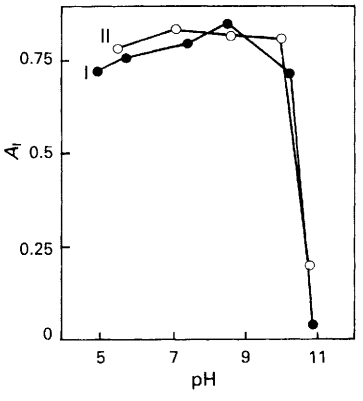

Fig. 1. pH ranges for the re-extraction of the UO_2 - PBH chelate. The pH was adjusted with dilute solutions of hydrochloric acid or sodium hydroxide: I, without NaCl; and II, with 0.2 M NaCl

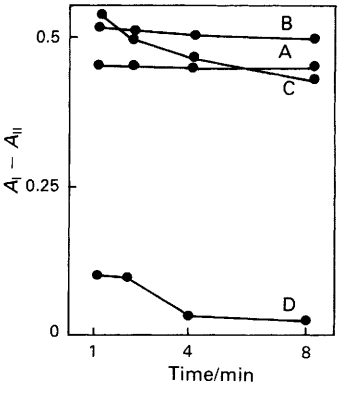

Fig. 2. Influence of the shaking time of the two phases and the mole ratio of ligand to metal in the organic phase for 100 μg ml^{-1} of carbonate in the aqueous phase [A_I, spectrophotometric blank, containing no carbonate; and A_{II}, samples containing 10 mg of carbonate in the aqueous phase (100 ml)]. PBH to UO_2 mole ratio: A, 15.7; B, 12; C, 7.8; and D, 4

Table 1. Precision of the method

Concentration of carbonate/ μg ml^{-1}	Absorbance* (at 510 nm)	Relative standard deviation, %
0	$A_I = 0.698$	0.3
40	$A_I - A_{II} = 0.158$	2.2
80	$A_I - A_{II} = 0.361$	0.6

* A_I = Absorbance of the re-extract without CO_3^{2-} in the aqueous phase; A_{II} = absorbance of the re-extract with 100 μg ml^{-1} of CO_3^{2-} added to the aqueous phase.

Table 2. Effect of foreign ions on the determination of total carbonate in binary mixtures (50 μg ml^{-1} as CO_3^{2-})

Ion tested	Concentration tolerated/ μg ml^{-1}
Thiosulphate, sulphate, bromate, acetate, nitrite, sulphite, bromide, benzoate, arsenate, tungstate, iodate, iodide, perchlorate, chromate, nitrate, Li^{I}, K^{I}, Mg^{II}, Ba^{II}	300
Borate, fluoride, thiocyanate, citrate, EDTA, persulphate, silicate, molybdate, Rb^{I}, Sr^{II}	150
Dichromate	100
Tetraborate	75
Oxalate, arsenite, hexacyanoferrate(II), tartrate, Ca^{II}, Sb^{III}, Au^{III}	30
Cyanide, sulphide, selenite, hexacyanoferrate(III), phosphate, Sn^{II}, Hg^{II}, Bi^{III}, Ag^{I}	15
Vanadate, Ce^{IV}, Ni^{II}	6
Periodate, Pb^{II}, Al^{III}, Cr^{III}, Cu^{II}, Tl^{I}, Fe^{II}, U^{VI}	1
Permanganate, Cd^{II}, Zr^{IV}, Fe^{III}, Rh^{III}, Mn^{II}, Zn^{II}, Co^{II}, Be^{II}	<1

Precision of the method

The reproducibility of the method (tested with three series of 11 samples and with a 95% confidence level) was evaluated and the results are presented in Table 1.

Interferences

A study of the effect of 66 other ions was carried out by preparing a series of synthetic samples containing 50 μg ml^{-1} of total carbonate and various amounts of the foreign ions according to the proposed procedure. Cations were added in the form of their chlorides, nitrates or sulphates and anions as their sodium, potassium or ammonium salts.

The maximum concentration of foreign ions tested was 300 μg ml^{-1} and the limiting value of the concentration of foreign ions was taken as that value which caused an error of not more than 4% in the absorbance.

The results obtained following the procedure for these binary mixtures are summarised in Table 2. As can be seen, the procedure is relatively free from interferences by anions; however, the tolerance limits for cations are lower (due to the added metal ions reacting with the excess of the ligand and being extracted into the organic phase), nevertheless they are adequate.

Determination of total carbonate in different samples

The reliability of the proposed method was tested by applying it to the determination of total carbonate in several types of sample (saline and non-saline). The samples used were: three different samples of sea water from Cádiz Bay (Spain) [the temperatures of the three samples (1, 2 and 3) were 25.3, 24.9 and 25.2 °C, respectively]; two bottled mineral waters ("Fontvella" and "Solan de Cabras") and two digestive pharmacological preparations "Alka-Seltzer" and "Eno").

Table 3. Comparison of re-extraction spectrophotometric and Gripenberg methods for the determination of total carbonate

Sample	CO_3^{2-} found/μg ml^{-1}* Gripenberg method	Re-extraction method	Error, %
Sea water 1	100.5	96.8	3.7
Sea water 2	119.1	114.3	4.0
Sea water 3	125.2	121.4	3.0
"Fontvella"	105.5	104.5	0.9
"Solan de Cabras"	264.7	288.1	8.8
"Alka-Seltzer"	665.0†	675.1	1.5
"Eno"	372.6†	374.7	0.6

* Values are the means of two determinations.
† As preparations.

The carbonate concentration was calculated using the calibration graph by following the described procedure and adding a known amount of water (mineral or sea water) or an aqueous solution of the pharmacological sample. The total carbonate concentration must be within the range 30–100 μg ml^{-1} in the aqueous phase. In order to obtain better results for the sea water samples, a synthetic sea water matrix[12] was employed to obtain the calibration graph so that the volumes of the samples and standards were the same. The results obtained were in good agreement with those obtained using the Gripenberg method (Table 3)[12]; the results were relatively good if it is borne in mind that the relative standard deviation of the method is between 0.3 and 2.2% (see Table 1). The error for the "Solan de Cabras" sample may be due to the presence of small amounts of silicate and arsenate, which would affect the alkalinity measurement in the Gripenberg method. The proposed spectrophotometric method does not suffer from this problem because these species do not interfere.

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