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Distribution of Traces During Precipitation of Barium Carbonate

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ABSTRACT

In this article, we investigate the distribution of traces of Na, K, Ca, and Sr during the fractionated precipitation of barium carbonate from barium chloride solution with ammonium carbonate. The results of trace distributions were determined with ^{24}Na, ^{42}K, ^{45}Ca, and ^{85}Sr isotopes. In a concentration range of 1×10^{-4} to 1×10^{-3} % (related to $BaCl_2$) at 80% of matrix precipitation the following quantities of trace impurities remained in the solution (%) Na: 89–94, K: 92–98, Ca: 38–47, and Sr: 35–26. The influence of DCTA complexing agent on impurities distribution was found to be insignificant. The distribution of Cd(II), Co(II), Cu(II), Fe(III),

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Mn(II), Ni(II), Pb(II), and Zn(II) in single-mode precipitation $BaCO_3$ with $(NH_4)_2CO_3$ was also investigated in the presence of EDTA and DCTA, and without any complexing agent. The AAS method was used to determine traces of heavy metal content. After a precipitation of 80% of matrix $BaCO_3$ in presence EDTA, and 1×10^{-4} % initial trace concentrations, the following quantities (%) of 55 Cd, 70 Co, 72 Cu, 52 Fe, 70 Mn, 83 Ni, 60 Pb, and 67 Zn remained in the solution. The results were used for the optimization of $BaCO_3$ obtainment.

Key Words: Crystallization; Barium carbonate; Distribution coefficients of impurities; Fractionated precipitation.

INTRODUCTION

The question of Na, K, Ca, and Sr removal from $BaCl_2$ solution is a part of research on high purity $BaCO_3$ obtainment. The literature survey on $BaCO_3$ obtainment and some methods of $BaCl_2$ solution purification was performed.[1–7] Barium chloride as a good soluble substance may be used as a substrate for high purity $BaCO_3$ production. Publications[8–12] deal with the problem by discussing crystallization, co-precipitation, and extraction methods. Barium compounds are usually contaminated by alkali, by related alkali earth metals, and by some heavy metals. The concentration and removal processes are then necessary in both the preparation and the analysis of high-purity barium compounds. Published research on high-purity $BaCO_3$ preparation is very rare[1–4] and the degree of purity achieved is not shown. The definition of high purity is also not clear, e.g., 99.99% is regarded as high.[4] Crystallization is applied to separate macroquantities of Ba from microquantities of Na, K, Ca, and Sr, while crystallization and extraction is used in the case of heavy metals.[5–10] Extraction allows for the easy separation of especially heavy metals as stable internal complex compounds.[11–13] However the efficiency and the purity of degree data are very difficult to find.

In this work, the distribution of traces of Na, K, Ca, and Sr during fractionated precipitation of barium carbonate using the radioactive indicators method was investigated. High sensitivity, selectivity, and safety are advantages of this method.[14] The distribution of coefficients of Ca and Sr during the process in the presence of 1,2 diaminecyclohexanetetraacetic acid diammonium salt (DCTA) are also examined. The distribution coefficients D (Henderson–Kraček) and λ (Doerner–Hoskins) of microcomponents during crystallization are important indicators of its effectiveness as a purification process.

The distribution of Cd, Co, Cu, Fe, Mn, Ni, Pb, and Zn was also investigated by single precipitation of $BaCO_3$ from the $BaCl_2$ solution with

$(NH_4)_2CO_3$. The environment of ammonium ions is favorable for soluble ammine complexes of Zn, Ni, Cd, Co, and Cu formation. Moreover, stable $CuCl_3^-$, $CuCl_4^{-2}$, $FeC1_4^-$, $CoCl_4^{2-}$ ions are formed in the presence of Cl^-.[15] Single precipitation of $BaCO_3$ in ethylenediaminetetraacetic acid disodium salt (Na_2-EDTA) and DCTA environment was also investigated. In this case, ions of trace elements react as follows:

$$M^{n+} + H_2Y^{2-} \leftrightarrows MY^{n-4} + 2H^+$$

Dissociation of this complex depends then on pH. When $BaCO_3$ precipitation is carried out at $pH = 8.5$, then the formation of stable chelates of the ions under investigation is expected, which may result in a small degree of trace co-precipitation.[16,17]

EXPERIMENTAL

Reagents and Apparatus

- Spectrally pure barium chloride from POCh, Gliwice, Poland.
- Ammonium carbonate, 3.0 M, solution obtained by saturation of redistilled water with gaseous ammonia and carbon dioxide in polyethylene flask.
- Hydrochloric acid, 36%, spectrally pure, from the Nitrogen Compounds Plant in Tarnów, Poland.
- Isotopes of sodium, potassium, calcium, and strontium from the Institute of Nuclear Research, Świerk near Warsaw.
- 1,2 Diaminecyclohexanetetraacetic acid diammonium salt.
- Ethylenediaminetetraacetic acid disodium salt.

The isotopes of sodium and potassium, obtained in the form of $^{24}Na_2CO_3$ and $^{42}K_2CO_3$, after dissolving in a small volume of water, were neutralized. Next 0.1-M HCl was added in a measuring flask with a volume of 50 ccm. The isotopes of calcium and strontium in the form of $^{85}SrCl_2$ and $^{45}CaCl_2$ solutions were placed in measuring flasks with a volume of 50 ccm applying 0.1-M HCl. The solutions' concentrations and the radioactive data of these isotopes are shown in Table 1. The basic standard solutions of cadmium, cobalt, copper, iron, manganese, nickel, lead, and zinc contain 1 mg of the element in 1 ccm. The standard solutions of the microcomponents were prepared by diluting the basic solutions, respectively. All the solutions were prepared by applying distilled water purified on an ion-exchange column and then distilled twice in a quartz apparatus.

Table 1. Basic solutions of applied radioactive isotopes and their characteristics.

	Symbol			
	^{24}Na	^{42}K	^{45}Ca	^{85}Sr
In its basic solution	^{24}NaCI in 0.1-M HCl	^{42}KCI in 0.1-M HCl	^{45}CaCI$_2$ in 0.1-M HCl	^{85}SrCI$_2$ in 0.1-M HCl
Concentration of the basic solution (mgM^{n+}/ccm)	1.70	2.25	1.00	1.10
Intensity of radiation of the basic solution (mCi/ccm)	0.20	0.20	0.02	0.02
Time of partial decomposition $\tau^{1/2}$	14.90 hr	12.46 hr	153 days	64.5 days
Kind of radiation	β^-, γ	β^-, γ	β^-	EC
Radiation energy				
β	1.400 (100%)	3.550 (82%)	0.256 (100%)	1.900 (78%)
γ	2.75 (100%)	1.52 (100%)	—	0.514 (99.3%)

Note: EC, electron capture.

- Atomic absorption spectrometer (AAS), Perkin Elmer 400, USA
- Geiger-Muller counter, AOH-45, USSR[a]
- Scintillation counter EKCO, Electronics Ltd[a]

ANALYTIC METHOD

Measurements of Radioactivity[a] and Absorbance

In these experiments, a barium chloride solution containing traces of the investigated radioactive element was used. During each experiment, from every batch of these solutions, six samples of $BaCl_2$ in a series, with a time, were taken. They were obtained by adding a specific amount of $(NH_4)_2CO_3$ to the mother liquor. The content of the given element (Na, K, Ca, Sr) was

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[a] The measurements were carried out on the apparatus at the Institute of Ferrous Metallurgy, 44-100 Gliwice, Poland.

determined by measuring the radioactive intensity. For this purpose, the analyzed sediments were placed in polyethylene phials with a lid and then in the niche (cavity) of the scintillation counter, composed from a NaI monocrystal activated by TI. Initially, it was found that the mass of the sediments does not influence the measurements of the radiation of sodium, potassium, and strontium. Radiometric measurements of ^{45}Ca were carried out making use of a Geiger-Müller counter with a window coupled with an electronic counter type EKCO. Deviations in the measurement of the radioactivity of calcium due to the absorption of β-particles by the counter window, as well as the air between the source and the counter window, may be neglected. It was possible because the conditions of measurements of the background, the standard samples, and the tested samples were the same. Deviations due to self-absorption of sediment, however, were taken into account, i.e., the mass of the analyzed sediment (the absorbing medium). The dependence of the self-absorption of the β-particles in the sediment on the mass of barium carbonate in the case of determining ^{45}Ca could be neglected. It was found that the mass of $BaCO_3$ in the range of 0.5–1.0 g does not effect the reckoning of the β-particles.

To determine the recovery coefficient of calcium during the fractionated precipitation of the matrix, standards were applied that contained the isotope ^{45}Ca in an amount of either 50 or 5 μg, deposited on 0.8 g barium carbonate. Similar standards were used to determine the recovery coefficient of strontium, sodium, and potassium. The total activity was calculated from the mean value of three measurements.

The recovery coefficient of the given investigated element was determined from the relation (taking into account the value of the background):

$$R\% = \frac{\text{Relative radioactivity of the sample}}{\text{Relative radioactivity of the standard}} \cdot 100\% \tag{1}$$

Based on the content of microcomponents in the obtained sediments, the following quantities could be calculated:
α, Rate of separation of the macrocomponent, where:

$$\alpha = \frac{\text{Amount of the separated macrocomponent}}{\text{Initial amount of the macrocomponent}} \tag{2}$$

β, Rate of co-precipitation of the microcomponent, where:

$$\beta = \frac{\text{Amount of the microcomponent in the sediment}}{\text{Initial amount of the microcomponent}} \tag{3}$$

D, λ, distribution ratios, where:

$$D = \frac{\beta(1-\alpha)}{\alpha(1-\beta)} \tag{4}$$

$$\lambda = \frac{\log(1-\beta)}{\log(1-\alpha)} \tag{5}$$

K, Degree of complete purification, where:

$$K = \prod_{i=1}^{n} k_i \tag{6}$$

$$k_i = \frac{\text{initial concentration of the microcomponent}}{\text{concentration of the microcomponent of the sediment after } i \text{ crystallization}} \tag{7}$$

Trace amounts of cadmium, cobalt, copper, iron, manganese, nickel, lead, and zinc were determined by means of the AAS method on the basis of the work of Korolewicz and Mazońska.[10] All mentioned samples and sets standards (prepared on the basis of high-purity $BaCl_2$), with barium chloride concentrations that were the same, were excited in flame and their absorbance measured under the same conditions. The results are presented in Table 2.

Conditions and Methods of Crystallization

The distribution of sodium, potassium, calcium, and strontium by fractionated precipitation of barium carbonate with ammonium carbonate was investigated. For this purpose the isotopes ^{24}Na, ^{42}K, ^{45}Ca, and ^{85}Sr were applied. These investigations were carried out for two initial concentrations of the microcomponents, viz, $1 \times 10^{-4}\%$ and $1 \times 10^{-3}\%$ as related to solid $BaCl_2$.

Every experiment was carried out as follows. To the 20 ccm of 1.5-M barium chloride solution 3.0-M ammonium carbonate was added. The precipitation of $BaCO_3$ was instantaneously observed. The suspension was mixed for 20 min and then solids were separated by filtration. Next, another portion of ammonium carbonate was added. This procedure was repeated five times. The whole process was carried out at a temperature of 20°C. The amount of the ammonium carbonate used was initially chosen in such a way that the mass of the successively separated solid phases would be approximately similar to each other. After having been filtered off, the obtained solid phases were rinsed twice on a funnel with 5 ccm of 1-M ammonium carbonate to avoid adsorption of impurities. The distribution of calcium and strontium ions

Table 2. Standard conditions of determination of microcomponents by AAS.

Element	Wavelength (nm)	Bandpass (nm)	Lamp intensity (mA)	Air-acetylene flow rate (dm^3/min)
Cd	228.8	0.7	6 w	11-1
Co	240.7	0.2	30	11-1
Cu	324.8	0.7	30	11-1
Fe	248.3	0.2	30	11-1
Mn	279.5	0.2	30	11-1
Ni	232.0	0.2	30	11-1
Pb	283.3	0.7	15	11-1
Zn	213.9	0.7	15	11-1

during the fractionated precipitation of $BaCO_3$ in the presence of DCTA was determined. The content of DCTA was 0.5% as related to $BaCl_2$. Such obtained solutions were then discarded. The sediment was dried and its radioactivity was measured as a function of time. In addition, the activity of standard samples was measured simultaneously. Based on the recovery coefficient [$R\%$] values obtained of the investigated elements, the values of α, β, λ, D, and K, were calculated. The results are gathered in Tables 3–5 and Figs. 1 and 2. It was found, that during the fractionated precipitation of $BaCO_3$ with ammonium carbonate, the ions of sodium and potassium and partially calcium, strontium are mostly retained in the liquor. It seemed to be expedient to investigate the distribution of heavy metals during the separation of the matrix.

The pH of the solutions were measured. During the addition of the next amounts of ammonium carbonate solution the pH was approximately constant and practically equal to 6 until the whole mass of macrocomponent was precipitated. It is caused by the obtained buffer solution.

The distribution of microamounts of Cd, Co, Cu, Fe, Mn, Ni, Pb, and Zn in the course of a single separation of the barium ions with ammonium carbonate was investigated. The solid phases were separated with ammonium carbonate from 1.5-M solutions of barium chloride at a temperature of 80°C. The contact time of the phases was 60 min. Initial concentrations of the investigated microcomponents were $1 \times 10^{-4}\%$. The distribution of heavy metals in single-mode precipitation $BaCO_3$ with $(NH_4)_2CO_3$ was also investigated in the presence of EDTA and DCTA. The content of DCTA and EDTA was 0.5% as related to $BaCl_2$. These were then cooled down.

Table 3. Distribution of sodium and potassium ions during the fractionated precipitation of the matrix with ammonium carbonate.

Investigated microcomponent	No. of the fraction	Initial concentration of the microcomponent $1 \times 10^{-3}\%$				Initial concentration of the microcomponent $1 \times 10^{-4}\%$			
		α	β	λ	D	α	β	λ	D
^{24}Na	1	0.149	0.0099	0.0616	0.0570	0.152	0.0132	0.0806	0.0746
	2	0.302	0.0211	0.0592	0.0497	0.296	0.0264	0.0762	0.0645
	3	0.446	0.0317	0.0546	0.0407	0.446	0.0402	0.0694	0.0520
	4	0.592	0.0400	0.0455	0.0287	0.590	0.0562	0.0648	0.0413
	5	0.729	0.0498	0.0391	0.0195	0.733	0.0750	0.0590	0.0295
	6	0.882	0.0608	0.0294	0.0087	0.868	0.1110	0.0582	0.0191
^{42}K	1	0.148	0.0051	0.0319	0.0295	0.147	0.0143	0.0906	0.0842
	2	0.285	0.0064	0.0191	0.0161	0.292	0.0256	0.0752	0.0638
	3	0.429	0.0077	0.0138	0.0103	0.437	0.0378	0.0671	0.0507
	4	0.571	0.0099	0.0117	0.0075	0.569	0.0458	0.0557	0.0363
	5	0.715	0.0128	0.0103	0.0052	0.712	0.0574	0.0475	0.0246
	6	0.850	0.0150	0.0080	0.0027	0.863	0.0824	0.0432	0.0142

Table 4. Distribution of calcium and strontium ions during the fractionated precipitation of the matrix with ammonium carbonate.

Investigated microcomponent	No. of the fraction	Initial concentration of the microcomponent $1 \times 10^{-3}\%$				Initial concentration of the microcomponent $1 \times 10^{-4}\%$			
		α	β	λ	D	α	β	λ	D
^{45}Ca	1	0.143	0.0870	0.590	0.571	0.139	0.0889	0.624	0.606
	2	0.290	0.194	0.629	0.588	0.285	0.237	0.808	0.781
	3	0.445	0.319	0.652	0.583	0.421	0.374	0.857	0.821
	4	0.590	0.418	0.607	0.499	0.573	0.519	0.858	0.802
	5	0.726	0.504	0.541	0.383	0.700	0.589	0.738	0.614
	6	0.848	0.534	0.405	0.205	0.830	0.620	0.547	0.335
^{85}Sr	1	0.137	0.159	1.176	1.192	0.131	0.0761	0.564	0.546
	2	0.265	0.255	0.956	0.949	0.268	0.157	0.546	0.507
	3	0.410	0.371	0.879	0.850	0.398	0.246	0.556	0.493
	4	0.542	0.492	0.867	0.817	0.542	0.355	0.563	0.466
	5	0.694	0.624	0.826	0.732	0.689	0.484	0.567	0.424
	6	0.830	0.739	0.756	0.577	0.844	0.655	0.573	0.351

Table 5. Distribution of calcium and strontium ions during the fractionated precipitation of the matrix with ammonium carbonate in presence of DCTA.

Investigated microcomponent	No. of the fraction	Initial concentration of the microcomponent $1 \times 10^{-3}\%$				Initial concentration of the microcomponent $1 \times 10^{-4}\%$			
		α	β	λ	D	α	β	λ	D
^{45}Ca	1	0.138	0.082	0.575	0.557	0.133	0.0937	0.690	0.674
	2	0.272	0.168	0.579	0.540	0.259	0.180	0.661	0.627
	3	0.400	0.260	0.589	0.527	0.403	0.266	0.598	0.536
	4	0.544	0.402	0.654	0.563	0.538	0.387	0.635	0.544
	5	0.698	0.562	0.689	0.555	0.691	0.519	0.624	0.483
	6	0.838	0.602	0.506	0.292	0.826	0.613	0.543	0.334
^{85}Sr	1	0.136	0.077	0.552	0.533	0.134	0.0775	0.561	0.543
	2	0.280	0.192	0.649	0.611	0.272	0.137	0.465	0.426
	3	0.417	0.275	0.599	0.533	0.416	0.255	0.549	0.483
	4	0.555	0.386	0.604	0.506	0.562	0.388	0.594	0.493
	5	0.696	0.519	0.617	0.474	0.708	0.532	0.617	0.471
	6	0.839	0.671	0.609	0.392	0.847	0.671	0.592	0.368

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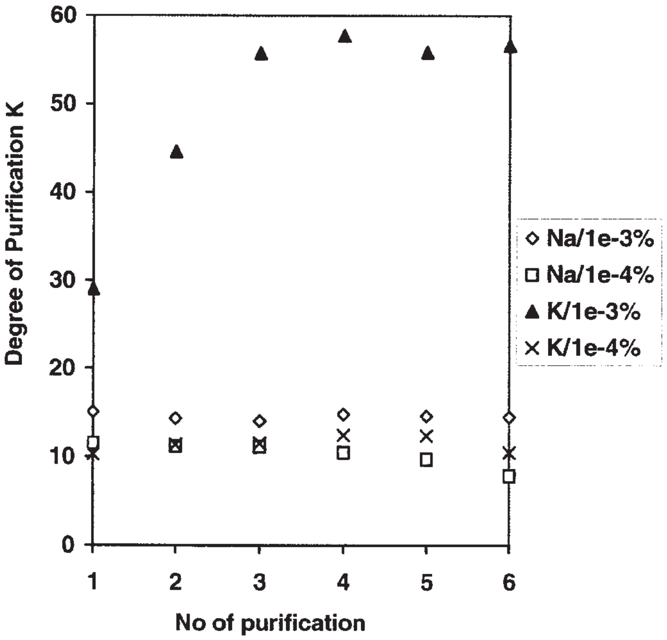

Figure 1. The dependence of degree of complete purification *K* on the number of co-precipitation; Na and K ions.

The sediments were separated and rinsed twice with 5 ccm of 1-M ammonium carbonate. The filtrate was neutralized, acidified with hydrochloric acid, and evaporated to dryness in Teflon beakers together with the solutions leftover after rinsing. The dry residue was placed in measuring flasks with a volume of 25 ccm each, applying 0.01-M hydrochloric acid. The content of trace elements was determined by means of the AAS method. The results have been gathered in Table 6.

RESULTS AND CONCLUSIONS

The results from investigations of the distribution of traces of sodium, potassium calcium, and strontium ions during the fractionated precipitation of $BaCO_3$ from $BaCl_2$ solution with $(NH_4)_2CO_3$ show that the co-precipitation process was neither homogeneous nor logarithmic (not constant values of λ and D coeficients as in Tables 3–5).[18]

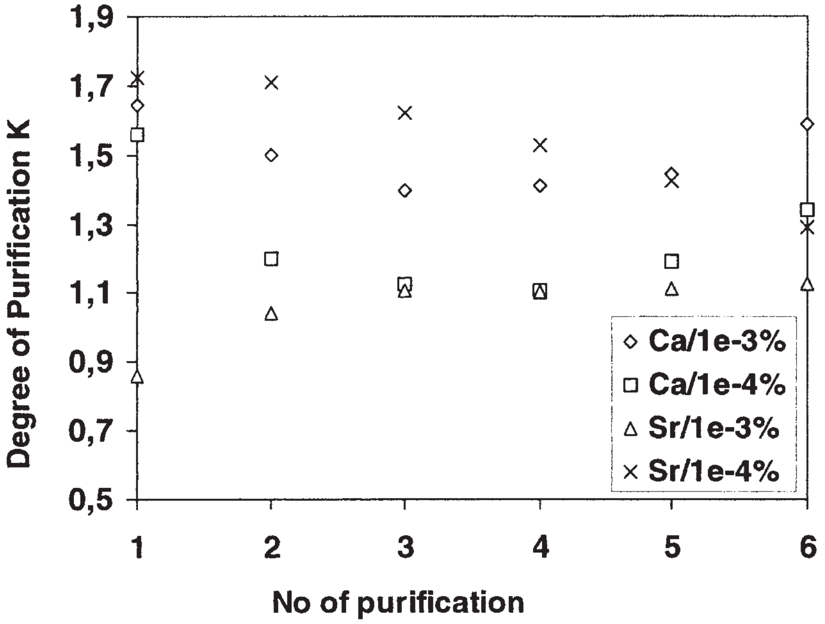

Figure 2. The dependence of degree of complete purification *K* on the number of co-precipitation; Ca and Sr ions.

The higher β values of co-precipitated strontium and calcium obtained, in comparison to sodium and potassium, could be the result of a similar value of ions radios Ca^{2+}, Sr^{2+}, i Ba^{2+} and smaller solubility of their carbonates. Applying the rinsing procedure twice after filtration of solid phases with 5 ccm of 1 M ammonium carbonate was to avoid the adsorption of impurities, so it could be assumed that the mechanism of the process was mainly co-precipitation.

The measured pH values (pH = 6) could only influence the coeficients λ and D for potassium and particularly, sodium production, because of the possibility of $NaHCO_3$ formation, but in the case of such a small concentration of microcomponent it cannot take place.

Within a concentration of 1×10^{-4} to $1 \times 10^{-3}\%$ (related to $BaCl_2$) at 80% of matrix precipitation, the following quantities of traces impurities remained in the solution (%) Na: 89–94, K: 92–98, Ca: 38–47, and S: 35–26 as in Tables 3 and 4. Applying DCTA as a complexing agent does not diminish co-precipitation of calcium and strontium ions (see Table 5). After a precipitation of 85% of matrix $BaCO_3$ in the presence of DCTA and

Table 6. Distribution of contaminations during of the precipitation of barium ions with ammonium carbonate from barium chloride solution.

	Precipitating agent $(NH_4)_2CO_3$		
Complexing agent	—	EDTA	DCTA
Initial content of impurities 1×10^{-4} (%)			
Amount of microcomponent remained in the solution (%)			
Cd	9	55	53
Co	47	70	68
Cu	70	72	70
Fe	8	52	41
Mn	10	70	72
Ni	75	83	89
Pb	18	60	67
Zn	55	67	68

1×10^{-4}–10^{-3}% initial traces concentration, the following quantities (%) of 33 Sr, 39 Ca remained in the solution.

Comparison of the λ and D coefficient values presented in Tables 4 and 5 shows their considerable variation, especially in the case of initial fractions and higher concentration of Sr (10^{-3}%). Without the presence of DCTA, the values of λ varied from 1.1761 to 0.7564, while in the presence of this chelating agent, the value of λ is almost invariable and equal to about 0.6. With regard to the D coefficient, its value varied from 1.1918 to 0.5774 without the presence of DCTA, while it varied from 0.5332 to 0.3916 in the presence of DCTA. In the case of Ca, this effect is not observed.

The degree of complete purification K at 1×10^{-3}% potassium concentration was very high and equal to 52.69, while at 1×10^{-4}% it was also quite good and was larger than 8. In the case of sodium ions dependence of K on the initial traces concentration was weak and for 1×10^{-4}% it was equal to 10, while for 10^{-3}%, was equal to 15, as at Fig. 1. For calcium and strontium ions, the K values are low, i.e., below 2. Especially for the strontium ions for 10^{-3}%, the K value was a little higher than 1 (see Fig. 2), while for the first fraction was even 0.86 (D and λ values are larger than 1, see Table 4), which means contamination of the solid phase. The high K values for Na, K, Ca, and Sr induced us to investigate separation of heavy metals [Cd(II), Co(II), Cu(II), Fe(III), Mn(II), Ni(II), Pb(II), and Zn(II)] during precipitation of $BaCO_3$ from $BaCl_2$ solution (see Table 6). In the course of a single precipitation, almost complete co-precipitation of Cd, Fe, Mn, and Pb was found, while Co, Cu, Ni, and Zn remained in the solution in the following amounts (respectively, %): 47, 70, 75, 55 (see Table 6). In the presence of EDTA and DCTA complexing agents, the amounts of heavy metals that remained in the solution were higher. Furthermore, the amounts of remaining heavy metals were almost the same in the case of both EDTA and DCTA, despite high differences in the values of the stability constants of their complexes.[19] During precipitation of $BaCO_3$ from $BaCl_2$ solution in the presence of Na-EDTA, the amounts of heavy metals that remained in the solution were as follows (%): Cd, 55; Co, 70; Cu, 72; Fe, 52; Mn, 70; Ni, 83; Pb, 60; Zn, and 67 (Table 7).

A comparison of the distribution of traces during crystallization of both $BaCl_2$[9] and $BaCO_3$ was then made. The values of degree of complete purification attained for Na, K, Ca, and Sr in $BaCl_2$ varied from about 10 to 120 (Fig. 3), while in the case of $BaCO_3$ from 0.86 to 15 (see Figs. 1 and 2; only in the case of potassium for the concentration of microcomponent equal to 10^{-3}% the K value reached 28–58). As to heavy metal traces, the amount of them that remained in the solution during $BaCl_2$ crystallization (see Table 7) was much higher than in the case of $BaCO_3$ crystallization (see Table 6). Comparison of K values for Na, K, Ca, and Sr, as well as heavy metals distribution during $BaCl_2$ and $BaCO_3$ crystallization, shows great significance of preliminary purification of the substrate. First purification of $BaCl_2$ and

Table 7. Distribution of contaminations during precipitation of barium ions with spectrally pure HCl from $BaCl_2$ solution.[9]

Content of microcomponents in the solution after the precipitation of the matrix (%)	Initial concentration of the microcomponents in $BaCl_2$ solution (%)				
	5×10^{-5}	1×10^{-4}	5×10^{-4}	1×10^{-3}	5×10^{-3}
Cd	100	100	100	100	100
Co	100	100	100	100	100
Cu	80	90	99	99	99
Fe	50	75	90	92	93
Mn	90	95	95	95	95
Ni	73	85	98	99	99
Pb	66	53	47	41	28
Tl	—	—	100	100	100
Zn	90	90	86	85	85

Note: "—" Below the limit detecting the element in defined conditions.

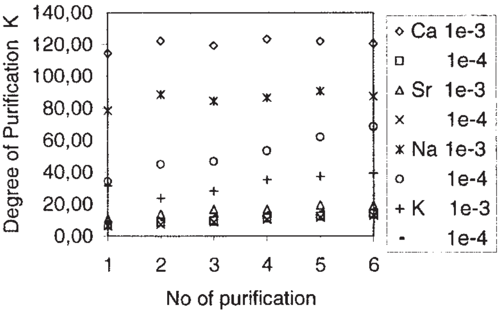

Figure 3. The dependence of degree of complete purification *K* on the number of co-precipitation; $BaCl_2$ crystallization.[9]

next, precipitation of $BaCO_3$, seems to be the optimal way of high-purity $BaCO_3$ preparation.

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