curves in Figs. 1 and 2. All three systems show type II solid solution according to the Roozeboom classification. Plotted also in Fig. 1 for comparison are data for the KBr–KCl–H_2O system as determined by Amadori and Pampanini[4] and by Flatt and Burkhardt.[5] The present results, which are more consistent than those of Amadori and Pampanini, indicate the congruent crystallization end-point to be at mole fraction 0.64 of potassium bromide as compared to the latters' value of 0.60. Although in this respect we agree with Flatt and Burkhardt, their results as compared with ours show a somewhat smaller fraction of potassium bromide in the liquid before this point, a larger one after.

The solubilities here reported for potassium chloride, potassium bromide and rubidium chloride are in excellent agreement with literature values.[11] That for rubidium bromide, 52.9%, is appreciably lower than the figure 53.7% given by Seidell,[11] which was interpolated by Fajans and Karagunis (see Meyer and Dunkel[12]) from measurements by Reissig[13] and Rimbach.[14] Rimbach's solubilities were obtained by means of the determination of bromide; if his rubidium bromide contained potassium bromide, this method of analysis would lead to high results.

Complexes 5A, 6A and 7A in the RbBr–KBr–H_2O system were prepared from rubidium bromide described in the RbBr–RbCl–H_2O system. Although the same weights of materials were used as in the respective B complexes, the compositions of the complexes differed due to the different percentage of potassium bromide present as impurity, and duplicate solid solutions would not be expected to result. The deviations actually found, however, are greater than can be attributed to this cause alone and are accompanied by a higher rubidium bromide content in the aqueous phase for the A complexes. On the basis of the agreement between the directly determined and the extrapolated solid-solution compositions, the A results seem as consistent analytically as the B. The reason for these differences is not known, although a possible explanation might be the presence of a small amount of soluble non-isomorphous impurity in the original rubidium bromide. Since it is felt that in these three cases the B results are probably the more dependable, they have been used in plotting the distribution curve.

Due to the indirect method of analysis coupled with the impurity of the rubidium salts, it is felt that the absolute error in the individual solid phase compositions may be as high as 1% for systems II and III. While this means that the distribution ratios in the dilute solutions may be relatively inaccurate, the accuracy is sufficient to fix satisfactorily the Roozeboom distribution curves.

Acknowledgment.—We are extremely grateful to the Society of the Sigma Xi for a Grant-in-Aid which made possible the purchase of the rubidium salts used in this research.

NORTHAMPTON, MASS.

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[11] A. Seidell, "Solubilities of Inorganic and Metal Organic Compounds," 3rd Edition, D. Van Nostrand Co., Inc., New York, N. Y., 1940, Vol. I, pp. 747, 684, 1429.

[12] K. Meyer and M. Dunkel, *Z. physik. Chem.*, Bodenstein Supplement, 556 (1931).

[13] T. Reissig, *Ann.*, **127**, 33 (1863).

[14] E. Rimbach, *Ber.*, **38**, 1553 (1905).

[CONTRIBUTION FROM THE GEOPHYSICAL LABORATORY, CARNEGIE INSTITUTION OF WASHINGTON]

The System H_2O–$NaPO_3$

BY GEORGE W. MOREY

RECEIVED JULY 24, 1953

The solubility relations in the system H_2O–$NaPO_3$ up to the melting point of $NaPO_3$ were determined by the closed tube method, and the vapor pressures of the saturated solutions at the invariant points and at 400 and 500° were also measured.

Most of the phase equilibrium work of the Geophysical Laboratory has dealt with silicate systems, but to one interested in silicates the chemistry of the phosphates also is of interest. In both cases the structural element is a tetrahedral grouping of four oxygens around a central positive ion, and the various compounds are formed by repeated polymerization in which an oxygen atom is shared by two structural groups. Both the silicates and the phosphates are glass-formers because of the tendency toward repeated polymerization of tetrahedral groupings. Many of the differences between the silicates and the phosphates can be related to the difference in radii of the positive ions. Because of this interest in the phosphates as compared with the silicates, studies of some phosphate systems are nearing completion, and this paper is a report on one of these studies.

There is nothing in the literature about the system H_2O–$Na_2O \cdot P_2O_5$ above 100°. The results below 100° included in Fig. 1 are recalculated from "International Critical Tables"[1]; the experimental work is that of Imadsu.[2] The experimental results listed in Table I were all obtained by the closed tube method. The solubilities below 400° were made in sealed glass tubes rotated in an oven which was provided with an automatic temperature control.[3] Runs above 400° were made in sealed glass tubes in an ordinary furnace without continuous rotation, but the tubes were inverted

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[1] "International Critical Tables of Numerical Data, Physics, Chemistry and Technology," Vol. 4, McGraw-Hill Book Co., Inc., New York and London, 1928, p. 237.

[2] Akira Imadsu, *Mem. Coll. Sci. Eng.* (Kyoto Imperial University), **3**, 257 (1912).

[3] F. C. Kracek, G. W. Morey and H. E. Merwin, *Am. J. Sci.*, **35A**, 143 (1938).

several times to make sure that equilibrium was attained. Temperatures were determined by a Pt–Pt90 Rh10 thermocouple, the bare junction of which was within a few mm. of the middle of the rotating tube. The glass tubes were Corning 702 glass and showed no attack except on runs of several days' duration. In many cases, the melting temperatures were repeatedly determined on the same sample by lowering the temperature until the melt crystallized and then again heating to the temperature at which crystals just disappeared.

TABLE I

SOLUBILITY RESULTS IN THE SYSTEM H_2O–$NaPO_3$

Wt. fraction $NaPO_3$	Liquidus temp., °C.	Primary phase
0.70	147	NaH_2PO_4
.739[a]	159	NaH_2PO_4
.765	210	$Na_2H_2P_2O_7$
.78	235	$Na_2H_2P_2O_7$
.794	256	$Na_2H_2P_2O_7$
.849[b]	305	$Na_2H_2P_2O_7$
.92	348	$Na_2H_2P_2O_7$
.93	402	$NaPO_3$II
.96	517	$NaPO_3$I

[a] Composition of $NaH_2PO_4 \cdot H_2O$. [b] Composition of NaH_2PO_4.

The inversion temperature of $NaPO_3$II, the invariant point G + L + $NaPO_3$II + $NaPO_3$I, was located by heating tubes containing 4% water and examining the product under the petrographic microscope. Runs made with either glassy $NaPO_3$ or $NaPO_3$II gave $NaPO_3$II at 443°, $NaPO_3$I at 445°. Under similar conditions, $NaPO_3$I did not change to II at 440° in three days, but with 5% H_2O did change in 5 days. This reluctance of a high temperature form to change to the lower temperature form is not unusual. The inversion temperature is 443 ± 1°, the pressure about 15 bars.

The incongruent melting of $Na_2H_2P_2O_7$ was located in a similar manner, using a mixture containing 92% $NaPO_3$ and made either from NaH_2PO_4 and $NaPO_3$ glass or from H_2O and $NaPO_3$II. Heated below 343°, these gave $Na_2H_2P_2O_7$; above 343°, they gave $NaPO_3$II. The reaction $Na_2H_2P_2O_7 \rightleftarrows G + L + NaPO_3II$ is thus fixed at 343 ± 1°. The incongruent melting of NaH_2PO_4, the reaction $NaH_2PO_4 \rightleftarrows G + L + Na_2H_2P_2O_7$, was similarly fixed at 169°. The reaction took place promptly.

Three-phase pressures at 400, 500 and 600° were determined by heating samples in a crucible with a perforated bottom in steam at varying pressures. Below the *P–T* curve of the equilibrium G + S = L, the mixture is in the two-phase region G + S and the powdered salt remains unaffected. Above the three-phase curve, the mixture is in the region G + L and the salt melts and runs through the crucible. The pressure equipment is that described by Morey and Hesselgesser[4] and was not adapted to close control at such very low pressures. The following three-phase pressures were so determined: 400°, 17 ± 0.5 bars; 500°, 10 ± 1 bars. The pressures at the quadruple points G + L + $Na_2H_2P_2O_7$ + $NaPO_3$II and G + L + $NaPO_3$II + $NaPO_3$I were located in a similar manner. Mixtures of the appropriate composition were heated at constant temperature and successively higher pressures until the transformation took place.

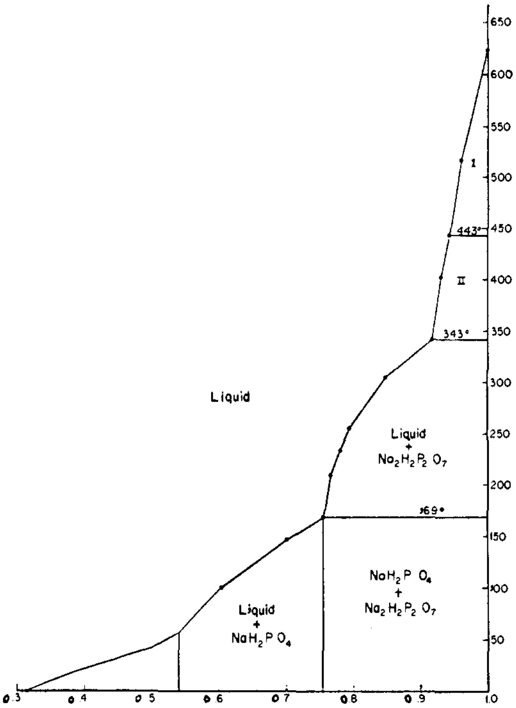

Fig. 1.—Solubility curve of the system H_2O–$NaPO_3$.

The Solid Phases

The optical properties of the solid phases found in the system are given in Table II. Unless otherwise stated, the optical properties are taken from Ingerson and Morey.[5] Table III shows the X-ray spacings in ångström units as determined by my

TABLE II

OPTICAL PROPERTIES OF COMPOUNDS

Formula	2*V*	Sign	α	ω	β	ε	γ
Ratio $H_2O:Na_2O:P_2O_5$ = 6:1:1							
$NaH_2PO_4 \cdot 2H_2O$	82°	−	1.4400		1.4625		1.4818
Ratio 4:1:1							
$NaH_2PO_4 \cdot H_2O$	29°	−	1.4557		1.4852		1.4873
$NaPO_3 \cdot 2H_2O$		−		1.441		1.432	
Ratio 2:1:1							
NaH_2PO_4	69°	−	1.481		1.507		1.517
$NaPO_3 \cdot H_2O$[a]		−	1.440		1.460		1.470
Ratio 1:1:1							
$Na_2H_2P_2O_7$[b]	61°	−	1.500		1.518		1.525
$2NaPO_3 \cdot H_2O$[c]			1.480		...		1.504
Ratio 0:1:1							
$NaPO_3$I	80°	−	1.474		1.478		1.480
$NaPO_3$II	78°	+	1.498		1.510		1.529
$NaPO_3$III[d]	70°	+	1.480		1.492		1.517
$NaPO_3$I′[d]		+		1.490		1.500	
$NaPO_3$I″	?	?	1.475?		...		1.520?

[a] Determined by Hall Laboratories. [b] Determined by C. Robbins. [c] Determined by G. W. Morey. [d] Determined by E. Ingerson.

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(4) G. W. Morey and J. M. Hesselgesser, *Econ. Geol.*, **46**, 821 (1951).

(5) E. Ingerson and G. W. Morey, *Am. Mineralogist*, **28**, 448 (1943).

TABLE III

X-RAY SPACINGS OF SOME OF THE SODIUM PHOSPHATE COMPOUNDS

$NaPO_3I$		$NaPO_3II$		$Na_2H_2P_2O_7$		NaH_2PO_4		$NaPO_3I$		$NaPO_3II$		$Na_2H_2P_2O_7$		NaH_2PO_4	
I^a	d, Å.	I^a	d, Å.	I^a	d, Å.	I^a	d, Å.	I^a	d, Å.	I^a	d, Å.	I^a	d, Å.	I^a	d, Å.
0.6	6.80	0.2	7.67	0.1	5.89	0.3	4.97	0.1	2.92	0.1	2.59	0.1	2.000	0.2	2.250
1.0	6.68	.2	7.06	.1	5.66	.6	4.78	.2	2.268	.5	2.534	.1	1.952	.2	2.246
0.5	5.10	.5	6.79	.1	5.39	.3	4.08	.2	2.205	.2	2.519	.2	1.852	.2	2.240
.8	5.03	.7	6.66	.4	5.04	.9	3.96	.2	2.176	.1	2.500			.1	2.227
.2	4.26	.5	5.37	.6	4.07	.3	3.67	.2	2.128	.1	2.457			.2	2.172
		.6	5.10												
.3	3.97	.9	5.04	.1	3.85	.2	3.54	.4	2.029	.1	2.406			.2	2.151
1.0	3.86	.1	4.24	.1	3.69	1.0	3.38	.2	1.983	.2	2.353			.3	2.138
.6	3.45	.2	3.96	.2	3.51	.8	3.30	.1	1.966	.3	2.294			.1	2.091
1.0	3.41	1.0	3.85	.7	3.45	.6	3.20	.1	1.954	.3	2.265			.1	2.048
.6	3.34	.5	3.52	.2	3.33	.2	3.17	.1	1.927	.1	2.203			.1	2.010
.2	3.12	.5	3.44	.3	3.30	.2	3.08	.2	1.910	.1	2.172			.2	1.976
1.0	3.04	.9	3.41	.7	3.10	.3	3.03	.2	1.871	.1	2.138			.1	1.947
.3	2.84	.5	3.35	1.0	2.93	.2	2.96	.2	1.850	.1	2.125			.1	1.919
.6	2.76	.5	3.33	.3	2.75	.2	2.84			.1	2.068			.1	1.890
.4	2.73	.5	3.29	.3	2.73	.1	2.77			.3	2.028			.1	1.872
.2	2.71	.5	3.12	.1	2.63	.7	2.72			.1	2.007			.2	1.854
.2	2.59	.2	3.09	.2	2.313	.1	2.59			.1	1.979			.2	1.849
.5	2.54	.8	3.04	.3	2.298	.1	2.539			.1	1.951			.2	1.845
.3	2.53	.5	2.89	.1	2.260	.1	2.516			.1	1.916			.2	1.840
.2	2.51	.2	2.83	.2	2.187	.2	2.486			.2	1.870			.4	1.834
.2	2.459	.5	2.76	.1	2.144	.2	2.396			.1	1.849				
.2	2.411	.6	2.72	.1	2.030	.1	2.300								

colleague J. L. England by the Debye–Scherrer powder method with a North American Philips high angle Geiger counter goniometer, using copper $K\alpha$ radiation and a nickel filter. The scanning was at one half degree per minute and the recording at two degrees per minute. The relative intensities I^a are based on a scale of ten. Following are comments on the indicated phases.

Phases of Ratio $H_2O:Na_2O:P_2O_5 = 6:1:1$.—The compound $NaH_2PO_4 \cdot 2H_2O$, sodium dihydrogen orthophosphate dihydrate, is solid phase from 0 to 40.8°, at which temperature it melts incongruently with formation of $NaH_2PO_4 \cdot H_2O$. No experiments were made with it.

Phases of Ratio 4:1:1.—The compound $NaH_2PO_4 \cdot H_2O$ is solid phase from 40.8 to 57.4°, at which temperature it melts incongruently with formation of NaH_2PO_4. When heated in a closed tube, the crystals of NaH_2PO_4 disappear at 159°, the melting point of a mixture of this composition.

The compound $NaPO_3 \cdot 2H_2O$ is obtained by dissolving $NaPO_3I$ in water and evaporating at room temperature. When the solution is heated it changes to a solution from which an orthophosphate separates.

Phases of Ratio 2:1:1.—Sodium dihydrogen orthophosphate, NaH_2PO_4, becomes primary phase at 57.4° and remains primary phase up to its incongruent melting point at 169°. The reaction at this invariant point is

$$NaH_2PO_4 = G + L + Na_2H_2P_2O_7$$

and the liquid contains 0.755 weight fraction $NaPO_3$. The vapor pressure is about 4.1 bars.

The compound $NaPO_3 \cdot H_2O$ was given me by Dr. A. E. R. Westman, Director, Department of Chemistry, Ontario Research Foundation. The optical properties were determined by the Hall Laboratories, Pittsburgh, Pennsylvania. I have not been able to prepare it. It also changes too rapidly on heating in a closed tube to realize an invariant point.

Phases of Ratio 1:1:1.—The compound $Na_2H_2P_2O_7$ is commonly known as disodium dihydrogen pyrophosphate. It is primary phase from 169 to 375°, at which temperature it melts incongruently with formation of $NaPO_3II$. The reaction at this invariant point is $Na_2H_2P_2O_7 = G + L + NaPO_3II$, with the pressure at about 12.5 bars. In the phase equilibrium diagram of the ternary system H_2O–Na_2O–P_2O_5, it is a binary compound in the system water–sodium metaphosphate, and its field (unpublished work) does not extend to the binary system water–sodium pyrophosphate. From this point of view, it would be called sodium metaborate hemihydrate, but, nevertheless, its solution in water gives the same ions as are formed with $Na_4P_2O_7$.[6]

Sodium metaphosphate hemihydrate, $2NaPO_3 \cdot H_2O$: This compound was obtained by evaporating a solution of $NaPO_3I$ in air in an attempt to prepare $NaPO_3 \cdot 2H_2O$. It forms excellent crystals of NaH_2PO_4 on heating in closed tube at 133°. The identification was made by X-ray, and there was no indication of another crystalline phase being present.

Phases of Ratio 0:1:1, Anhydrous Sodium Metaphosphate.—Several forms of crystalline sodium metaphosphate have been described, some of which have been prepared in connection with this study. Following are some comments on these various forms.

$NaPO_3I$, "trimetaphosphate," is the form ordinarily obtained on cooling a melt and crystallizing above 443°. It is quickly dissolved by water.

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[6] A. E. R. Westman, A. E. Scott and Joan T. Pedley, *Chemistry in Can.*, 35 (189) (October, 1952).

$NaPO_3II$, "Madrell salt," is obtained by crystallizing the glass just below 443°. Obtained in this way, it rarely is well crystallized, but when obtained with aid of water, it usually gives well-formed crystals. "Madrell salt" is the stable phase from the incongruent melting of $Na_2H_2P_2O_7$ at 375 to 443°, at which temperature it changes to $NaPO_3I$. The conversion of $NaPO_3I$ to $NaPO_3II$ in the dry way is difficult and even is slow with the aid of 4% water. It will, however, change to II when heated with water in a sealed tube for a few days within the stability range of $NaPO_3II$. It dissolves very slowly in water.

$NaPO_3III$.—This was obtained by Liddell[7] as an insoluble residue from glassy $NaPO_3$ devitrified at 300°. The optical properties were determined by Earl Ingerson.[8]

$NaPO_3I'$.—This also was prepared by Liddell,[7] and the optical properties were determined by Ingerson.[8] The preparation and the X-ray pattern were confirmed in this Laboratory. A second form, $NaPO_3I''$, was described by Liddell, but we have not been able to prepare it by the method described, and accordingly no more information on it is available than is given in Liddell's paper.

"Kurrol Salt."—Huber and Klumpner[9] have given directions for the preparation of this form of crystalline $NaPO_3$, and Liddell has confirmed the preparation.

There are listed above six forms of crystalline $NaPO_3$, and a seventh form, otherwise unknown, is listed in the A.S.T.M. card index of X-Ray Diffraction Data, First Supplementary Set, II-1725 (1945). The only ones of known stability are those listed above as $NaPO_3I$ and $NaPO_3II$. The others may have a region of stability or may be metastable or monotropic, but to establish the facts would be difficult.

WASHINGTON, D. C.

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[7] Robert W. Liddell, THIS JOURNAL, **71**, 207 (1949).

[8] Private communication.

[9] Hans Huber and Karl Klumpner, *Z. anorg. allgem. Chem.*, **251**, 213 (1943).

[CONTRIBUTION FROM THE WM. H. NICHOLS LABORATORY OF NEW YORK UNIVERSITY]

The Solubilities of the Strontium Halates

BY WILLIAM F. LINKE

RECEIVED MAY 8, 1953

The eutectic of the system $Sr(ClO_3)_2$–H_2O lies at −37.0° and 54.5% $Sr(ClO_3)_2$, with $Sr(ClO_3)_2 \cdot 3H_2O$ and ice as solids. The transition from trihydrate to anhydrous salt occurs at 10°; a saturated solution boils at 121° and contains 68.7% $(SrClO_3)_2$. The composition of the trihydrate was confirmed by the change in its solubility at −20° when $SrBr_2$ was added to the solution. The eutectic of the system $Sr(BrO_3)_2$–H_2O is at −2.18° and 17.50% $Sr(BrO_3)_2$, with $Sr(BrO_3)_2 \cdot H_2O$ and ice as solids. The transition from monohydrate to anhydrous salt occurs at 75.5°, and a saturated solution boils at 104° and contains 41.0% $Sr(BrO_3)_2$. $Sr(IO_3)_2 \cdot H_2O$ and $Sr(IO_3)_2 \cdot 6H_2O$ precipitate from saturated solutions and do not decompose when isolated, but above 6° both are metastable with respect to the anhydrous salt. From the intersections of the solubility curves, the stable transition from hexahydrate to anhydrous salt has been found to occur at 6°, and the metastable transition from hexa- to monohydrate at 20.8°.

Tri-, penta- and octahydrates of strontium chlorate have been reported, and several allotropic modifications of the anhydrous salt are also listed.[1] The solubility of the anhydrous salt has been determined only at 18°. The solubility of monohydrated strontium bromate was determined at 15° by Rammelsberg, and at 18° by Kohlrausch, but little else is known of the hydrates or solubility relations of the salt. The mono- and hexahydrates of strontium iodate are well known, but their relative stabilities, and that of the anhydrous salt have not been investigated. The solubilities reported by earlier investigators do not agree with that found by Colman-Porter and Monk,[2] and various authors[2,3] report anomalies in the preparation of the monohydrate.

Materials

Strontium Chlorate.—A chloric acid solution was prepared from roughly equivalent quantities of C.P. $Ba(ClO_3)_2$ and H_2SO_4, and small amounts of BaO and H_2SO_4 were then added until no significant tests for Ba^{++} or $SO_4^{=}$ were obtained. C.P. $SrCO_3$ (which was previously leached with a large volume of boiling water) was then added until present in excess. The mixture was filtered, and evaporation by boiling yielded pure white anhydrous $Sr(ClO_3)_2$. The solution did not bump during the evaporation. The solid was recrystallized from water, air-dried, and stored at room temperature. The crystals seemed somewhat moist, and upon standing for several days some of them formed droplets of solution. Potilitzyn[1] has said that $Sr(ClO_3)_2$ is not deliquescent unless it contains $SrCl_2$, but no Cl^- ion was detected when $AgNO_3$ was added to a solution of the salt. A qualitative flame test showed that no sodium, and only traces of calcium were present. Analysis by reduction to chloride and Volhard titration showed 99.6% $Sr(ClO_3)_2$. Loss in weight upon drying at 110° was 0.26%.

$Sr(ClO_3)_2 \cdot 3H_2O$ was prepared by cooling a concentrated solution of the anhydrous salt in an acetone–Dry Ice-bath. When the solution had become very viscous, vigorous scratching produced the trihydrate. The excess solution was removed by suction, and the moist solid was stored at 7°.

Strontium Bromate.—The monohydrate was prepared from $Ba(BrO_3)_2$, H_2SO_4 and $SrCO_3$ in the same manner as the chlorate. The solution of $Sr(BrO_3)_2$ was evaporated, and in sharp contrast to the behavior of $Sr(ClO_3)_2$, the solid formed a cake on the bottom of the beaker and caused violent bumping. The salt cake was broken up only with difficulty, and the crystals showed strong triboluminescence when scratched. The salt was recrystallized from water and air-dried. Iodometry showed 95.2% $Sr(BrO_3)_2$ (calcd. for $Sr(BrO_3)_2 \cdot H_2O$ 95.0%). Loss in weight at 110° was 4.89% (calcd. 4.99%).

Strontium Iodate.—The monohydrate was prepared by mixing equivalent quantities of C.P. $SrCl_2 \cdot 6H_2O$ and HIO_3

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[1] For original references to older work, see: J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. II, Longmans, Green & Co., New York, N. Y., 1932, and Gmelin, "Handbuch der anorganischen Chemie," Vol. 29, Strontium, 1931.

[2] C. A. Colman-Porter and C. B. Monk, *J. Chem. Soc.*, 1812 (1952).

[3] S. Peltier and C. Duval, *Anal. chim. acta*, **1**, 355 (1947).