

TABLE 2. Dielectric constant and polarisation of thorium salicylate solutions at 25°.

Mole fraction of $\text{ThO}(\text{Sal}^-)_2$	d_4	ϵ	n_D	$P_{1,2}$	P_2	$R_{1,2}$	R_2
0.00000	1.0280	2.208	1.4200	24.60	—	21.69	—
0.00071	1.0307	2.222	1.4206	24.84	360.4	21.75	103.2
0.00145	1.0336	2.236	1.4212	25.08	357.5	21.80	101.7
0.00222	1.0367	2.252	1.4218	25.34	357.1	21.86	100.0
0.00254	1.0378	2.258	1.4221	25.44	357.2	21.89	102.1
0.00300	1.0398	2.267	1.4225	25.60	356.9	21.93	100.8

The dielectric constant (ϵ), density (d), and refractive index (n_D), and the calculated values of the total polarisation and refraction of the solutions ($P_{1,2}$, $R_{1,2}$) and dissolved substance (P_2 , R_2) are given in Table 2. $P_\infty = 359 \text{ cm}^3$ and $R_\infty = 103 \text{ cm}^3$ by extrapolation. Thus, the dipole moment is

$$\mu = 0.22 \sqrt{P_\infty - (R_\infty + P_A)} = 3.43 \text{ D};$$

which indicates considerable polarity in the thorium salicylate molecule.

SUMMARY

The thorium nitrate-sodium salicylate-water system has been studied. The electrical conductivity and pH of the liquid phase have been measured. It has been shown that thorium nitrate undergoes double decomposition with sodium salicylate in the molar ratio 1:2. The composition of the product, which is sparingly soluble in water, depends on the duration of contact between the precipitate and the supernatant liquor. When the reagent solutions are mixed, the product is anhydrous thorium salicylate $\text{ThO}(\text{Sal}^-)_2$, which is gradually converted into $\text{ThO}(\text{Sal}^-)_2 \cdot 3\text{H}_2\text{O}$.

Thorium salicylate has been studied by chemical and thermographic analysis and its density and dipole moment have been determined.

1. Sbornik "Analiticheskaya Khimiya Urana i Toriya" (Collected Papers: The Analytical Chemistry of Uranium and Thorium) (Translated into Russian), Inostr. Lit., Moscow, 1956, p. 239.
2. D.I. Ryabchikov and E.K. Gol'braikh, Uspekhi Khim., **28**, 408 (1959).
3. G.T. Seaborg and J.J. Katz, "The Actinide Elements" (Translated into Russian), Inostr. Lit., Moscow, 1955.
4. H. Brinzinger and F. Jahn, Z. anorg. Chem., **235**, 115 (1937).
5. L. Moser and J. Singer, Monatsh., **48**, 673 (1927).
6. G.B. Wengert, R.C. Walker, M.F. Loucks, and W.A. Stenger, Analyt. Chem., **24**, 1636 (1952).
7. M. Therald and P. Wenkata, J. Amer. Chem. Soc., **75**, 3946, 3949 (1953).
8. M. Bobtelsky and B. Graus, J. Amer. Chem. Soc., **75**, 382 (1953).
9. M. Dittrich and S. Freund, Z. anorg. Chem., **56**, 344 (1908).
10. W.W. Wendlant, Analyt. Chem., **29**, 800 (1957).
11. A.C. Neish, J. Amer. Chem. Soc., **26**, 780 (1904).
12. H. Brintzinger and F. Jahn, Z. anorg. Chem., **235**, 115 (1937).
13. O.E. Zvyagintsev and V.N. Sudarikov, Zhur. Neorg. Khim., **1**, 69 (1956).

14. Ya.A. Fialkov and N.K. Davidenko, Ukrain. Khim. Zhur., **25**, 147 (1959).
15. A. Kolb and A. Ahrle, Z. angew. Chem., **18**, 98 (1905).
16. A.C. Neish, Chem. News, **90**, 192 (1904).
17. S.T. Morgen, J. Pharmacol., **73**, 472 (1904).
18. B. Hok-Bernström, Acta Chem. Scand., **10**, 174 (1956).
19. K.N. Kovalenko and M.N. Tarasova, Zhur. Neorg. Khim., **5**, 385 (1960) [Russ. J. Inorg. Chem., 184 (1960)].

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COMPLEX FORMATION IN NIOBIUM(V)-SALICYLATE-ORGANIC BASE SYSTEMS

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There are few data on the salicylate-complexes of niobium $^{5+}$, and none on ternary mixed complexes of niobium with salicylic acid and different amines. We have studied the formation and properties of niobium salicylate and ternary Nb-Sal-organic base complexes.

Preliminary experiments showed that solutions containing $1.6 \times 10^{-3} \text{ M}$ niobium and a 10- to 15-fold excess of sodium salicylate at pH 4 do not give a precipitate of niobium hydroxide, but a soluble yellow complex of niobium with salicylic acid is formed. The absorption spectrum of niobium salicylate and the dependence of the optical density of niobium salicylate solutions on the pH and salicylic acid concentration were studied. 0.5 ml 0.65 M potassium niobate containing 8 M KOH was treated with a 100-fold excess of sodium salicylate, after which 1 M HCl was added to establish the required pH, which was measured with an LP-5 pH-meter and glass electrode. The solutions were diluted with water to 100 ml. Their colour developed gradually, but showed no further change after 10 min. At $\text{pH} < 2.5$ they became turbid. The pH dependence of the optical density of niobium salicylate at 380 μm , 390 μm , and 400 μm is shown in Fig. 1.

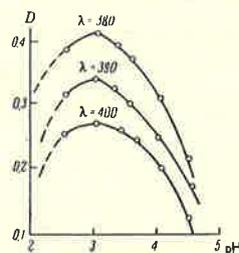


Fig. 1. pH dependence of the optical density of niobium salicylate:
 $[\text{Nb}] = 3.25 \times 10^{-4} \text{ M}$; $[\text{NaHSal}] = 3.25 \times 10^{-2} \text{ M}$.

The absorption spectrum of niobium salicylate at pH 3.9 in the ultra-violet region is shown in curve 1 in Fig.2, with the absorption spectrum of sodium salicylate for comparison (curve 2 in Fig.2). When the niobium salicylate spectrum was recorded, a sodium salicylate solution with corresponding concentration and pH was used as reference solution. Fig.2 shows an absorption maximum for niobium salicylate at $\lambda = 330 \text{ m}\mu$. At $\lambda = 330 \text{ m}\mu$ and below, however, salicylic acid begins to absorb, so that it is more convenient to measure the optical density of niobium salicylate solutions in the visible region.

To study the influence of salicylic acid concentration, we prepared solutions containing the same quantity of niobium and different excesses of salicylic acid. The dependence of the optical density of niobium salicylate solutions on the sodium salicylate concentration at pH 3.9 (Fig.3) shows that at a niobium concentration $[\text{Nb}] = 0.65 \times 10^{-3} \text{ M}$, almost all the metal is bound in the complex at $[\text{Sal}] \approx 5 \times 10^{-2} \text{ M}$, i.e. with a 100-fold excess.

The data in Fig.3 were treated by the equilibrium displacement method and the results were used to construct the plot of $-\log(c_{\text{complex}}/c_{\text{Nb}_{\text{free}}})$ vs. $-\log[\text{HSal}]$, which proved to be linear, with $\tan \alpha = 2$ (Fig.4), so that at pH = 3-4 a complex with an $[\text{Nb}]:[\text{Sal}]$ ratio of 1:2 is formed.

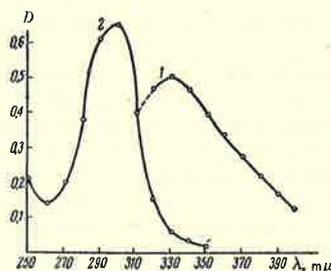


Fig.2. Absorption spectrum of niobium salicylate in the ultra-violet range: pH 3.3, $[\text{Nb}] = 3.2 \times 10^{-3} \text{ M}$, $[\text{NaHSal}] = 6.4 \times 10^{-2} \text{ M}$; 1) niobium salicylate; 2) sodium salicylate.

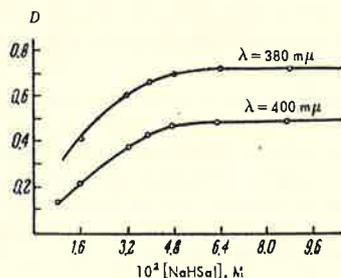


Fig.3. Dependence of the optical density of niobium salicylate on the salicylic acid concentration; pH 3.9, $[\text{Nb}] = 0.65 \times 10^{-3} \text{ M}$.

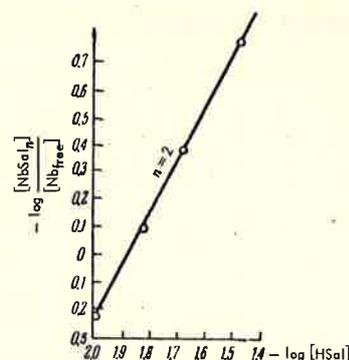
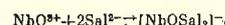


Fig.4. Dependence of the degree of complex formation by niobium on the sodium salicylate concentration.

The data in Fig.3 for $\lambda = 380 \text{ m}\mu$ were used to calculate the equilibrium constant for the formation of the salicylato-niobium complex. This can be represented by the following general equation, if we assume that the niobium not combined in the complex exists in solution as NbO^{3+} :



The concentration of the complex was calculated from the formula $c = D/\epsilon d$, where $\epsilon = 1100$. The numerical value of ϵ was determined under conditions where the niobium was completely bound in the salicylato-complex, at pH 3.9 and $\lambda = 380 \text{ m}\mu$. The equilibrium concentration of niobium not combined in the complex was found from the difference $[\text{Nb}_{\text{equil}}] = [\text{Nb}_{\text{total}}] - [\text{Nb}_{\text{complex}}]$. The total equilibrium concentration of salicylic acid was found from the total salicylic acid concentration by subtracting twice the concentration of the complex:

$$[\text{Sal}_{\text{total equil}}] = [\text{Sal}_{\text{total}}] - 2[\text{Nb}_{\text{complex}}]$$

At pH 3.9 the greater part of the salicylic acid uncombined in the complex is present as the HSal^- ion, so that the equilibrium concentration $[\text{Sal}^{2-}]$ was calculated from the formula

$$[\text{Sal}^{2-}] = \frac{K_2}{[\text{H}^+]} \times [\text{Sal}_{\text{total equil}}]$$

The results were used to calculate the instability constant of the complex

$$K_{\text{NbOSal}_2} = \frac{[\text{NbO}^{3+}][\text{Sal}^{2-}]^2}{[\text{NbOSal}_2^-]}$$

The results are given in the Table. In all experiments the total niobium concentration was $0.65 \times 10^{-3} \text{ M}$, $I = 0.04$, and $t = 25^\circ$. The mean value is $K_{\text{NbOSal}_2} = 2.5 \times 10^{-23}$.

These data are only approximate, since the state in solution of uncombined niobium is unknown. The electromigration of the salicylato-complex of niobium at pH 3-4 showed that the coloured layer moves towards the anode, so that the complex can be represented

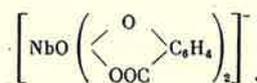


TABLE. Calculation of the instability constant of the complex.

Total concentration 10^{-4} [H ₂ Sal], M	D_{380}	10^4 [Nb _{complex}]	10^4 [Nb _{equiv}]	10^{11} [Sal ²⁻]	10^{23} K _{NbCSal₂}	Total concentration 10^{-4} [H ₂ Sal], M	D_{380}	10^4 [Nb _{complex}]	10^4 [Nb _{equiv}]	10^{11} [Sal ²⁻]	10^{23} K _{NbCSal₂}
1.0	0.275	2.5	4.0	0.4	2.6	3.2	0.610	5.5	1.0	1.2	2.6
1.6	0.410	3.7	2.8	0.6	2.7	4.2	0.660	6.0	0.5	1.6	2.1

Conditions for the Formation of Ternary Nb-Sal-Organic Base Complexes

When certain organic bases are added to a solution containing niobium and salicylic acid, sparingly soluble, yellow ternary complexes are formed which are readily extracted by chloroform. The formation of ternary niobium complexes depends chiefly on the pH and reagent concentrations. At the optimum values of pH = 3, total niobium concentration [Nb] = 1.3×10^{-3} M and [NaHSal] = 1.3×10^{-1} M, a 4- to 10-fold excess (relative to Nb) of the organic base is sufficient for almost complete extraction of niobium by chloroform. Of the ten organic bases which we studied, the strongest, triethylamine ($pB = 3.3$) and quinine ($pB_1 = 6$; $pB_2 = 9.9$), extract niobium completely even in small (4- to 5-fold) excess. A slightly larger excess is required for diantipyrylmethane ($pB = 13$) and pyramidon† ($pB = 9.2$), presumably because at pH = 3 the stronger bases are present as cations which form salts with $[\text{NbOSal}_2]^-$, whereas the weak bases are still to a considerable extent present in the free form. The completeness of the extraction depends considerably on the solubility of the salt of the base with the salicylatoniobic acid, so that there is no direct relationship between the degree of extraction and the strength of the base. Thus the largest excess of base is required in the case of urotropine ($pB = 9.1$) and antipyrine ($pB = 9.1$), whose basic strengths are about the same as that of pyramidon, but which differ sharply from the latter in their ability to extract niobium salicylate.

Usually an optimum concentration of base in the aqueous phase is reached, after which further addition produces no change in the degree of extraction. In some cases (quinine, codeine, and to a lesser extent diantipyrylmethane), an excess of the base even decreases the extraction of niobium because some bases react with salicylic acid to give salts which are sparingly soluble in water and readily soluble in chloroform, so that the concentration of salicylic acid in the aqueous phase is decreased and becomes insufficient to bind the niobium in the complex. The decrease in the optical density of the extract in the presence of an excess of the base (Fig. 5) may also be due to the extraction of a complex of different composition.

The salicylic acid concentration has a very marked effect on the extraction of the ternary niobium complex, and a considerable excess is required for complete extraction of the metal. For most of the bases, not more than 8-15% of the niobium was extracted for a 10- to 20-fold excess of sodium salicylate, relative to Nb. Transition to

† 4-Dimethylamino-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one; aminopyrine (Ed. of Translation).

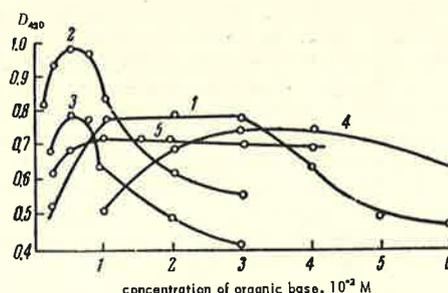
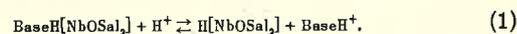


Fig. 5. Dependence of the optical density at $\lambda = 420 \text{ m}\mu$ for an extract of the ternary niobium complex on the concentration of organic base: [Nb] = 1.3×10^{-3} M, [NaHSal] = 1.3×10^{-1} M, pH 2.5-3. Bases: pyramidon (1), antipyrine (4), quinine (2), codeine (3), and triethylamine (5).

the horizontal section (optimum conditions) is usually observed at $[\text{Sal}_{\text{total}}] = 0.1$ M. 0.06 M sodium salicylate is sufficient only with pyramidon and codeine, evidently due to the low solubility of their salts with the complex salicylatoniobic acid. Some examples are given in Fig. 6.

pH has a marked effect on the extraction of the ternary complexes. The colour of the Nb-Sal complexes of all the bases is destroyed at pH > 3-3.5. The stability of the complex in more acidic medium depends on the base. The narrowest pH range is shown by the strong aliphatic bases tetralin‡ and triethylamine (curves 5 and 6 in Fig. 7b) and the highest stability is observed for the weakest base, diantipyrylmethane. Acidification should intensify the displacement of the cation of the free base from its salt with the formation of free acid



At the same time, however, the excess of weak base present in solution in the free form is mainly converted into the cation



For diantipyrylmethane ($pB = 13$) at pH 1 (i.e. at $\text{pH} = 14 - pB$) there is a particularly sharp displacement of equilibrium (2) to the right, leading to a sharp increase in the concentration of BaseH^+ cations; this in turn displaces equilibrium (1) to the left. Thus the compound formed by diantipyrylmethane with niobium salicylate is stable even in 1 N HCl, whereas most of the bases form salts which decompose at pH 1.

The solubility of the salt in chloroform is also important. Thus it was pointed out above that pyramidon appears to give a much less soluble compound than hexamethylenetetramine (urotropine). Although the values of pB for these bases are almost identical, the pyramidon compounds are much more stable than the urotropine compounds (curve 1 in Fig. 7a and curve 10 in Fig. 7d).

‡ Sic; presumably not tetrahydronaphthalene (Ed. of Translation).

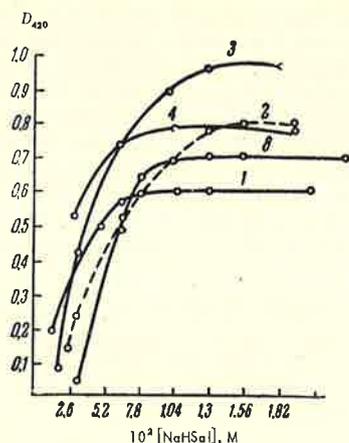


Fig. 6. Dependence of the optical density at $\lambda = 420 \text{ m}\mu$ for an extract of the ternary niobium complex on the salicylic acid concentration: $[\text{Nb}] = 1.3 \times 10^{-3} \text{ M}$, pH 2.5 - 3. Bases: pyrimidin (1), antipyrine (4), quinine (2), codeine (3), and pyridine (5).

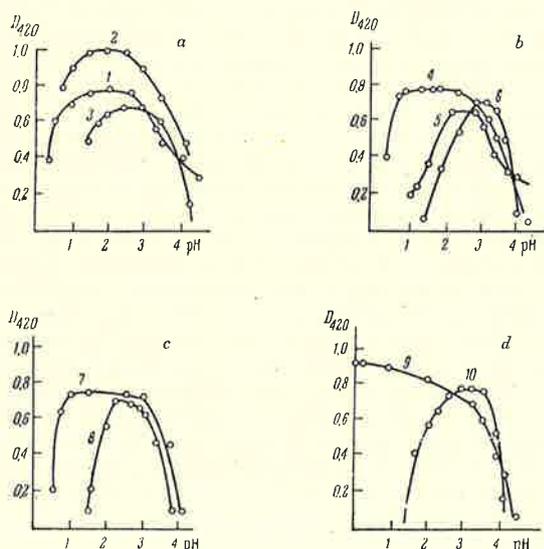


Fig. 7. pH dependence of the optical density of extracts of the ternary niobium complexes at $\lambda = 420 \text{ m}\mu$ and $[\text{Nb}] = 1.3 \times 10^{-3} \text{ M}$. Bases: a) pyrimidin (1), quinine (2), codeine (3); b) antipyrine (4), triethylamine (5), tetralin (6); c) quinoline (7), pyridine (8); d) diantipyrilmethane (9), hexamethylenetetramine (10).

The shape of the curves in Fig. 7 indicates fairly complete extraction of niobium under optimum conditions of $[\text{Base}]$, $[\text{NaHSal}]$, and pH. To confirm this we carried out a number of control experiments in which the niobium remaining in the aqueous phase after a single extraction was determined by the thiocyanate method. For pyrimidin,

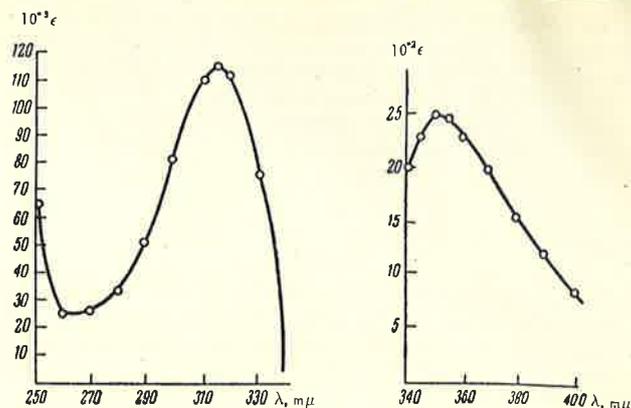


Fig. 8. Absorption spectrum of a chloroform extract of the ternary Nb-Sal-organic base complex: niobium concentration in extract $[\text{Nb}] = 3.2 \times 10^{-4} \text{ M}$, pH 2.7.

pyridine, and triethylamine, it was found that an equal volume of chloroform under optimum conditions extracts 93-99% of the niobium in a single stage; the curves giving the pH dependence of the extraction of niobium are completely analogous to those in Fig. 7. The higher value of the optical density for some of the bases (quinine, diantipyrilmethane, etc., Fig. 7) is thus due not to more complete extraction of niobium but to other optical properties. This in turn appears to be due to a difference in the Nb:Sal ratio in the complexes being extracted.

The absorption spectrum of a chloroform extract of the ternary Nb-Sal-pyridine complex is shown in Fig. 8. A 100-fold excess of sodium salicylate and pyridine was added to 0.4 ml 0.02 M potassium niobate and the pH was brought to 2.7 by means of 1 N HCl. The niobium was $3.2 \times 10^{-4} \text{ M}$. The solution was extracted two or three times with 5 ml portions of chloroform until a colourless extract was obtained. The absence of niobium in the aqueous phase was confirmed by the thiocyanate test. Under these conditions niobium is completely extracted by chloroform. The extracts were combined and diluted to 25 ml with chloroform in a graduated flask, after which the optical density was measured. A solution with pH 2.7, containing sodium salicylate and pyridine at the same concentrations but no niobium was used as reference solution. Analogous absorption spectra were obtained for the complexes of niobium salicylate with a number of other bases.

The ternary niobium complex shows an intense band at $\lambda = 315 \text{ m}\mu$ (Fig. 8). In the figure the different bands are shown on different scales for the sake of clarity. The high density of the complex in the range $\lambda = 310-315 \text{ m}\mu$ is due to absorption by salicylic acid in this range, which makes it unsuitable to use this absorption band for photometric analysis. The extract of excess reagents (NaHSal and base) gives the same band whether niobium is present or not. At $\lambda = 340 \text{ m}\mu$, however, salicylic acid absorbs very little light, and the absorption is proportional to the quantity of niobium. In this range the mean value of the molar extinction coefficient of the ternary complex is $\epsilon = 2530$.

§ Triethylamine? (Ed. of Translation).

By constructing calibration curves for niobium concentrations in the range 2×10^{-4} to 12×10^{-4} M at $\lambda = 350$ m μ , 400 m μ , and 420 m μ , it was established that the ternary niobium complex can be used to determine niobium in the presence of tantalum and other elements which do not form coloured ternary complexes with salicylic acid and organic bases.

SUMMARY

1. The physicochemical characteristics and conditions of formation of the yellow salicylatoniobium complex have been studied. At pH 3 a complex anion with Nb:Sal ratio = 1:2 is formed. The instability constant of the complex at pH 4 is

$$K_{\text{NbOSal}_2} = \frac{[\text{NbO}^{3+}][\text{Sal}^{2-}]^2}{[\text{NbOSal}_2^-]} = 2.5 \times 10^{-23}$$

2. Ternary complexes, which can be extracted with chloroform, are formed in niobium-salicylate-organic base systems. The following organic bases have been studied: pyridine, quinoline, pyrimidin, antipyrine, diantipyrylmethane, quinine, codeine, hexamethylenetetramine, triethylamine, and tetralin. The formation of ternary niobium complexes is determined chiefly by the pH and reagent concentrations. The optimum pH is 2-3. In more strongly acidic medium, the stability of the complex depends on the nature of the base. The absorption spectrum of a chloroform extract of the ternary niobium complex shows two absorption bands: one at $\lambda = 315$ m μ due to salicylic acid and one at $\lambda = 350$ m μ due to niobium. The latter can be used for the photometric determination of niobium.

1. B. N. Sudarikov and Yu. I. Busarov, Zhur. Neorg. Khim., 2, 702 (1957).
2. O. N. Morozova, "Khimiya Redkikh Elementov" (The Chemistry of the Rare Elements), GONTI, 1957.

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THERMAL DECOMPOSITION OF OXALIC ACID AND BIVALENT METAL OXALATES

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It is well known that when oxalates are heated they decompose without sintering or melting, but this has not so far been sufficiently studied.

The thermal decomposition of oxalic acid and bivalent metal oxalates has been investigated in the present work by means of thermographic and other methods of physicochemical analysis.

An apparatus was employed which is a combination of a torsion balance and a Kurnakov thermal analysis apparatus; this permits the simultaneous recording of differential thermal and gravimetric curves as the temperature changes, which facilitates the interpretation of the results¹. A Pt-Pt-Rh thermocouple was used for the differential analysis and ignited aluminium oxide was employed as standard. With the small specimens, 40-50 mg, a high rate of heating (about 15 deg min⁻¹) can be used, although the temperature of some of the effects is then somewhat raised².

"Analytical reagent" grade oxalic acid, and oxalates of calcium, strontium, barium, and lead were used, and were analysed for metal oxide, oxalate ion, and water; their compositions were: H₂C₂O₄·2H₂O, CaC₂O₄·H₂O, SrC₂O₄·2H₂O, BaC₂O₄·7H₂O, PbC₂O₄.

The results (Fig. 1) show that the substances containing water begin to decompose endothermically at about 100°, and the compound changes weight. The thermogravimetric curve and analysis of the gaseous products (Table 1) show that the oxalic acid and calcium oxalate are completely dehydrated but strontium oxalate loses only one and barium oxalate two of their water molecules. The final dehydration occurs in the second endothermic reaction at about 200° when one water molecule is eliminated from strontium oxalate and five from barium oxalate (Table 1).

Thus the dehydration of strontium and barium oxalates, unlike that of calcium oxalate and oxalic acid, is a stepwise process accompanied by the absorption of heat at each stage. Anhydrous oxalic acid decomposed completely and endothermically on heating to 180° (Fig. 1a), with the liberation of steam, carbon monoxide, and carbon dioxide (Table 1). Further decomposition of the anhydrous oxalates of calcium, strontium, and lead occurs above 400°. The thermograms (Figs. 1b-1d) show that this decomposition is accompanied by two parallel reactions, one exothermic and the other endothermic, and by a change in weight of the salt. As regards the amount of heat liberated or absorbed, these reactions differ according to the composition of the salts, and this is reflected in the shape of the differential thermocouple curves. For example, whereas both the exothermic and endothermic effects are clearly expressed with calcium oxalate, with barium oxalate the endothermic effect is shown by the presence of only a small minimum at ~450° on the thermogram and it coincides with a maximum on the differential curve. With strontium oxalate the endothermic effect can be seen only from the truncation of the maximum

TABLE 1.

Substance	Temperature range of reaction, °C	Change in weight of salt from thermogram results, %	Gas analysis results, mole
H ₂ C ₂ O ₄ ·2H ₂ O	80-120	28.6	2H ₂ O
	190-220	71.4	H ₂ O, CO ₂ , CO
CaC ₂ O ₄ ·H ₂ O	150-260	12.3	H ₂ O
	450-510	19.2	CO
	790-900	30.1	CO ₂
SrC ₂ O ₄ ·2H ₂ O	50-130	8.5	H ₂ O
	180-220	8.5	H ₂ O
	480-510	13.3	CO
BaC ₂ O ₄ ·7H ₂ O	100-180	10.2	2H ₂ O
	230-260	25.7	5H ₂ O
	420-460	8.0	CO
PbC ₂ O ₄	350-400	24.5	CO ₂ , CO