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I. NOTES ON SODIUM COLUMBATES. II. THE ATOMIC WEIGHT OF COLUMBIUM.

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I. Notes on Sodium Columbates.

Little is known concerning the constitution of the columbic acids, hence their salts, the columbates, are usually expressed in the old dualistic form. Thus the general formula of the sodium columbates may be written: $x\mathrm{Na_2O}.y\mathrm{Cb_2O_5}.z\mathrm{H_2O}$. If we are to accept all the various ratios recorded in the literature, $x:y$ may vary from 4 to 0.25.[1] However, many of these salts were undoubtedly derived from impure material, while others were probably mixtures that happened to approach atomic ratios. The present investigation was restricted to the 7:6 and 1:1 ratios.

The former ratio was fully established by Bedford,[2] working in this laboratory, and confirmed by Balke and Smith.[3] They prepared the salt $7\mathrm{Na_2O}.6\mathrm{Cb_2O_5}.31\mathrm{H_2O}$ by different methods which had already been used by H. Rose, Hermann, and others, but had failed to give this particular salt. The 1:1 ratio had also been reported by Rose, but rested on questionable evidence, as was pointed out by Balke and Smith. These

[1] Abegg, "Handbuch," III, 3.

[2] THIS JOURNAL, **27**, 1216 (1905).

[3] *Ibid.*, **30**, 1644 (1908).

investigators allowed the mother liquors from the 7:6 salt to evaporate spontaneously and obtained a well-defined salt having the composition $Na_2O.Cb_2O_5.7H_2O$ (metacolumbate). They also determined its crystal habit, which has been very helpful in the present work.

The simple ratio and definite crystalline form of the 1:1 salt suggested its use for a redetermination of the atomic weight of columbium. Before this was undertaken, however, it seemed desirable to ascertain whether this compound could really be obtained sufficiently pure; that is to say, whether it was liable to be contaminated by the 7:6 salt, whether it was capable of recrystallization; and finally, as it was to be obtained from the mother liquor of another salt, whether any definite relation existed between these two salts.

For this part of the investigation some pure potassium oxyfluocolumbate was available which had been prepared, in this laboratory, by W. H. Chapin, in connection with his work on tantalum.[1] A quantity of this salt, dissolved in hot water, was mixed, in a large platinum dish, with three times its weight of pure sodium hydroxide (from sodium) dissolved in the least possible amount of water. This represents a large excess of alkali, but, as several failures indicated, this amount was practically necessary for the end in view. The heavy, white precipitate, which was insoluble in the excess of sodium hydroxide, was washed by decantation, filtered by suction, and washed with small quantities of cold water until a considerable portion of the columbate had been carried into the filtrate; this was noticed by a fresh precipitate being formed in the original filtrate containing the excess of alkali. The washed precipitate was then dissolved in boiling water and allowed to crystallize; this gave the 7:6 sodium columbate. Several preparations of the salt were made by this method, and it was soon noticed that the yield was conditioned by the amount of alkali used and the thoroughness exercised in washing the original precipitate. That is to say, a proportion of alkali smaller than that indicated above, followed by a very thorough washing, would produce little or no 7:6 salt; whereas a large excess of alkali and a rather superficial washing would increase the yield. This seemed to indicate that the formation of this salt was facilitated by a little free alkali in solution. This view was also supported by the fact that the crystallization could be hastened by the addition of a little sodium hydroxide, or carbonate, to a solution of the well-washed precipitate. The significance of this circumstance will appear below.

The 7:6 salt was recrystallized from boiling water and the mother liquor combined with that from the preceding crystallization. The combined liquids were allowed to evaporate spontaneously in a large platinum dish. After several weeks, large and well-defined crystals

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[1] Thesis, Univ. of Penna., 1909.

appeared; they resembled those obtained by Balke and Smith, and proved to be the 1 : 1 salt.

Analysis: 0.4719 g. of salt lost 0.1292 g. on ignition; 0.6604 g. of salt gave 0.3889 g. of columbic oxide, and 0.2046 g. of normal sodium sulfate, or:

		Calculated.	Found.
Na_2O.........	62	13.65%	13.53%
Cb_2O_5.........	266.2	58.61	58.80
$7H_2O$.........	126	27.74	27.59
	454.2	100.00%	99.92%

In analyzing these columbates the columbium was precipitated from a hot solution of the salt by the addition of dilute sulfuric acid. The filtrate was evaporated to dryness and ignited so as to form normal sodium sulfate. Only a very slight excess of the acid was used, otherwise much columbium was carried into the sodium sulfate.

Difficulty was encountered in attempting to recrystallize the 1 : 1 salt from water; usually the product was partly amorphous and far from uniform. Only one attempt was successful. In this instance the salt was dissolved in water of about 65°, the solution protected from the carbon dioxide of the air, and allowed to crystallize, under atmospheric pressure, over concentrated sulfuric acid.

Analysis of the recrystallized salt: 0.4850 g. of salt lost 0.1357 g. on ignition; 0.5574 g. of salt gave 0.3264 g. of columbic oxide, and 0.17733 g. of sodium sulfate, or:

		Calculated.	Found.
Na_2O.........	62	13.65%	13.58%
Cb_2O_5.........	266.2	58.61	58.56
$7H_2O$.........	126	27.74	27.98
	454.2	100.00%	100.12%

The following data may serve to point out the chief differences between the 7:6 and the 1 : 1 salt:

The 7:6 salt crystallizes in definite needles or slender prisms, often microscopic in size. It is difficultly soluble even in hot water. Upon ignition it becomes lemon-yellow in color, the latter deepening with increase of the temperature; it becomes white again on cooling. When heated it begins to cake somewhat, but does not melt, even at 1000°. The ignited mass appears to be insoluble in water, but part of its alkali splits off, leaving the 1 : 1 salt, according to the reaction:

$$7Na_2O.6Cb_2O_5 \rightleftarrows 12NaCbO_3 + Na_2O$$

As the sodium hydroxide seems to exert a solvent action on the metacolumbate produced, this reaction was not very sharp when the mass was extracted with water alone. A somewhat better result was obtained by extracting with dilute hydrochloric acid. Even in this case a small amount of columbic hydroxide appeared in the filtrate upon the addition of ammonium hydroxide; it was neglected, and this fact probably accounts for the low result.

Analysis: 1.5042 g. of 7:6 salt lost 0.4124 g. on ignition; another sample of the same salt weighing 1.3953 g. was extracted with dilute hydrochloric acid; the residue weighed 1.0454 g.

	Calculated.	Found.
$12NaCbO_3$ (insoluble).....	76.06%	74.92%
$1Na_2O$ (soluble)........	2.39	....
$31H_2O$..................	21.55	21.52
	100.00%	

The 1:1 salt, on the other hand, crystallizes in well-defined, short, stout, triclinic[1] crystals which, under favorable conditions, may grow to be 6–7 mm. in length. When allowed to crystallize under the microscope, the salt makes its appearance in diamond-shaped, or "coffin"-shaped forms, differing very distinctly from the needles of the former columbate. It is much more soluble than the 7:6 salt. It carries seven molecules of water of crystallization, the greater part of which (about 5 molecules) can be driven off on the steam bath. On ignition it also becomes yellow, but does not cake, even at 1000°. Strangely enough the crystals, when heated, do not fall to a powder, but merely shrink, retaining their original form and becoming quite hard. Water has no perceptible action upon this ignited mass and remains neutral in reaction; this test easily distinguishes this salt from the former.

As Bedford[2] has shown, the 7:6 salt can be thrown out of solution by alcohol. It was thought that the metacolumbate might be precipitated in a similar manner and thus be purified. However, when a solution of the 1:1 salt was treated with an excess of alcohol a mixture was precipitated. When absolute alcohol was added slowly, with constant stirring, in quantities sufficient to increase the original solution by one-third, a crystalline precipitate appeared which, under the microscope, resembled the 7:6 salt. Its analysis gave the following results:

0.2408 g. of salt lost 0.0523 g. on ignition; 0.2771 g. of salt gave 0.1702 g. of columbic oxide, and 0.1063 g. of sodium sulfate; or:

	Calculated for		Found.
	1:1 salt.	7:6 salt.	Salt by alcohol.
Na_2O........	13.65%	16.76%	16.75%
Cb_2O_5........	58.61	61.69	61.53
H_2O.........	27.74	21.55	21.72
	100.00%	100.00%	100.00%

The close summation is, of course, merely accidental. The result ad-

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[1] Balke and Smith, *loc. cit.*, p. 1651.

[2] THIS JOURNAL, **27**, 1217 (1905).

mits of no doubt that alcohol really produced this peculiar change, which, in its simplest form, may be expressed as follows:

$$7(Na_2O.Cb_2O_5) = 7Na_2O.6Cb_2O_5 + Cb_2O_5$$

In other words, in addition to the precipitate, columbic acid, or more likely, an acid columbate was probably formed which was not precipitated by a moderate amount of alcohol. An excess of the latter precipitated practically everything in solution and thereby produced the mixture referred to above. Some other neutral substances, likewise, seem to precipitate the 7:6 salt, the less soluble compound, from a solution of the meta-salt. Thus a solution of sodium chloride produces a crystalline precipitate resembling the 7:6 salt; its composition, however, was not determined.

From the preceding observations it may safely be concluded that the two sodium columbates discussed, the 7:6 and the 1:1 salts, are mutually convertible, and that their relation may be expressed by the reversible reaction:

$$7Na_2O.6Cb_2O_5 \rightleftarrows 6(Na_2O.Cb_2O_5) + Na_2O$$

In water solution this change must be assumed to take the form of a partial hydrolysis, as follows:

$$7Na_2O.6Cb_2O_5 + H_2O \rightleftarrows 6(Na_2O.Cb_2O_5) + 2NaOH$$

This suggested the use of carbon dioxide for hastening the reaction to proceed from left to right. When carbon dioxide was passed through the solution of the 7:6 salt the hydrolysis seemed to go beyond the 1:1 stage. However, when the solution was slowly condensed on the water bath, while an atmosphere of carbon dioxide was maintained *above* the liquid, a good yield of the 1:1 salt could be obtained. This method was finally used in the atomic weight determinations and will be mentioned again in Section II. It may be added that carbon dioxide does not, at any time, produce a turbidity in a solution of a pure columbate, even when the latter is exposed to the gas for many hours. This fact seems to prove conclusively that Rose's columbates must have been contaminated by other elements (probably by titanium or tantalum, or both), for he asserts that he obtained a gelatinous precipitate by[1] the action of carbon dioxide.

The mother liquors from the 1:1 salt may yield still other columbates, more acid than those discussed. However, as the acid content increases, the solubility seems to increase also, and these salts are crystallized with difficulty. In one instance the mother liquor from the 1:1 salt was allowed to evaporate spontaneously. An analysis of the resulting crystals indicated a salt between the ratios 3:4 and 4:5. It may be interesting to note that in another case the mother liquor from the 1:1 salt was evaporated to

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[1] *Pogg. Ann.*, **136**, 367 (1869).

dryness, ignited, and fused with sodium carbonate. A fresh crop of 7:6 salt was obtained, allowed to remain, as crystals, in the liquid, and the whole exposed to the action of carbon dioxide as explained before. Excellent crystals appeared after concentrating and cooling; they proved to be the 1:1 salt. Analysis:

0.5489 g. of salt lost 0.1526 g. on ignition; 0.4660 g. of salt gave 0.2732 g. of columbic oxide, and 0.1422 g. of sodium sulfate; or:

	Calculated for 1:1 salt.	Found.
Na_2O	13.65%	13.42%
Cb_2O_5	58.61	58.63
$7H_2O$	27.74	27.80
	100.00%	99.85%

The experimental data seem to prove that the 7:6 and 1:1 sodium columbates are two distinct and well-defined salts, and that they are mutually convertible. Undoubtedly other ratios do exist. It seems reasonable to suppose, however, that some of the rather improbable ratios recorded in the literature, and the failure of some chemists, like Marignac,[1] to obtain any definite sodium columbates, are to be attributed to the susceptibility of these salts to progressive hydrolysis together with the influence of carbon dioxide and free alkali, all of which factors might easily lead to the production of mixtures.

II. The Atomic Weight of Columbium.

The earliest determinations of the atomic weight of columbium are due to Rose, Hermann, and Blomstrand; the values obtained by these chemists are, today, of little more than historical interest. The researches of Marignac led to the first acceptable figure, about 94, which stood unchallenged for over fifty years. These earlier determinations need not be discussed here. A brief criticism of them may be found in Abegg's "Handbuch;" they are also commented upon by Balke and Smith in the paper "Observations on Columbium."[2] The only modern determination was made by the last-named investigators; they obtained an average of 93.50 for this element.

Balke and Smith made use of the ratio $2CbCl_5:Cb_2O_5$, established by the hydrolysis of the pentachloride. Their columbium was undoubtedly of high purity; however, certain other factors may have influenced the ratio. Thus, for example, the pentachloride is liable to retain traces of oxychloride. Furthermore, the residual oxide may have retained chlorine; this seems quite probable from the recent work of Sears and Balke[3] on the atomic weight of tantalum by a similar method. Both of these factors would tend to give too high an atomic weight. Finally, a slight volatiliza-

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[1] *J. Chem. Soc.*, **97**, 453 (1866).

[2] THIS JOURNAL, **30**, 1644 (1908).

[3] *Ibid.*, **37**, 840 (1915).

tion of columbium may have taken place, for, according to Hall and Smith[1] columbic oxide is volatile with hydrochloric acid gas; this would tend to lower the atomic weight. If the latter effect influenced the ratio, in addition to the first two, it is idle to conjecture as to which of these factors finally turned the balance. In any case, the value obtained by this method must be looked upon as somewhat uncertain, and a new determination by an entirely different method did not seem out of order.

It was decided to use sodium metacolumbate as a starting-out material, for the observations recorded in the first part of this paper point to this as the only sodium salt at all desirable for the end in view. As Hall[2] had been able to decompose native columbates by means of sulfur monochloride, it was to be expected that this reagent would effect the decomposition of a sodium columbate also, thus leading to the ratio $NaCbO_3$: NaCl. This was found to be actually the case, although the method required certain modifications. These will receive due notice after a brief description of the preparation and purification of the chief reagents used.

Some crude potassium fluocolumbate was on hand; it had originally been prepared by Hall[3] from South Dakota columbite. This salt was purified by methods that have been in use in this laboratory for some time and have been found to give pure columbium.[4] Suffice to say that this double fluoride was recrystallized five times from rather strong (1:1) hydrofluoric acid which had been redistilled for the purpose from potassium fluoride and a little silver phosphate. The salt was then converted into the oxyfluoride, and baked and recrystallized alternately; this process was also repeated five times. Platinum vessels and centrifugal draining were used throughout. The salt was then decomposed with concentrated sulfuric acid which had been redistilled from a retort of hard glass. The resulting columbic hydrate was thoroughly washed, first with water, and finally with a dilute solution of ammonium carbonate. The latter had first been digested with a little pure columbic hydrate and filtered; it was then used as indicated. After a prolonged washing the columbium hydroxide was obtained free from sulfates. This preparation was proved to be free from titanium by the salicylic acid reaction:[5] the absence of tantalum had been established by the well-known crystallization test.[6]

Sodium carbonate was purified in the following manner: A good C. P. grade was fused with a little pure, precipitated calcium carbonate; traces of silica, iron, etc., were thus rendered insoluble. The melt was disintegrated with water, filtered, and treated with carbon dioxide. The sodium

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[1] *Proc. Am. Phil. Soc.*, **44**, 197 (1905).

[2] Thesis, Univ. of Penna., 1904.

[3] Hall and Smith, THIS JOURNAL, **27**, 1369 (1905).

[4] *Ibid.*, see also Balke and Smith, *loc. cit.*

[5] J. H. Müller, THIS JOURNAL, **33**, 1508 (1911).

[6] *Proc. Am. Phil. Soc.*, **44**, 180 (1905); THIS JOURNAL, **27**, 1372 (1905).

bicarbonate produced was drained by centrifugal force and reprecipitated twice as the acid salt; it was now ready for use.

For the preparation of the metacolumbate the ignited columbic oxide was mixed with five to six times its weight of the sodium bicarbonate, ignited gently, and finally fused. Contrary to some statements a perfectly clear fusion can be brought about in this manner. After disintegrating the melt with water, sodium columbate remained as a heavy, white precipitate, insoluble in the excess of alkali. This was washed as indicated in Section I. It may be mentioned that no trace of sulfuric acid could be detected in this alkaline filtrate, showing that the columbic oxide had been free from this contamination. The well-washed mass thus obtained was crystallized, in a large platinum dish, from boiling water; this gave a small amount of 7:6 salt. The mother liquor from the latter was placed in a platinum dish and slowly condensed on the water bath. In the meantime an atmosphere of carbon dioxide was maintained above the liquid. The solution was stirred frequently, and a drop removed from time to time and allowed to crystallize under the microscope. Finally nothing but the characteristic, well-defined crystals of the 1:1 salt were noticeable when the drop had evaporated almost to dryness. By this time the solution had been condensed to about one-half its original volume. The liquid, which was entirely clear, was then cooled, inoculated with a trace of 1:1 salt from a previous preparation, and allowed to crystallize. Small but excellent crystals of the 1:1 salt were obtained. Under the microscope they appeared entirely uniform and free from inclusions or alterations of any sort. The crystals were washed several times with small quantities of cold water, being drained centrifugally after each washing. They were finally dried in air free from carbon dioxide. Several attempts were made to recrystallize this salt from water, but with little success. The product always suffered, except in one case, from one defect or another. It was finally decided to use the well-washed salt without recrystallizing.

The columbium of this salt must have been of high purity. It seemed possible, however, that the preparation might be contaminated with traces of either an acid columbate, or with free alkali, the latter being present as such or resulting from a trace of 7:6 salt on ignition. (See Section I.) The presence of an acid columbate was highly improbable on account of its greater solubility, and because of the care exercised in crystallizing the salt. That the amount of free alkali, if present at all, must have been exceedingly small seems to be indicated by the following tests: A powdered and ignited sample of the metacolumbate, weighing about one gram, was extracted with a cubic centimeter of hot water; the extract had no effect on very sensitive litmus paper. When a similar portion was boiled up with a small quantity of water, a drop of phenolphthalein would only produce an extremely faint pink color; no color was noticeable in the cold. Another sample of the ignited salt was extracted with dilute alcohol, the extract acidified with hydrochloric acid and evaporated to dryness. When water was added and the liquid tested with silver nitrate only a very faint opalescence appeared. Undoubtedly traces of the salt itself dissolved under these conditions, hence the degree of opalescence could not serve as an indirect measure for any free alkali in the salt. The tests seem to show, however, that the metacolumbate must have been reasonably free from traces of 7:6 salt and from uncombined alkali.

The sulfur monochloride was prepared by the action of dry chlorine upon dry, molten sulfur contained in a retort. The sulfur had been resublimed for the purpose; the chlorine was generated by the action of pure hydrochloric acid on potassium permanganate. The sulfur monochloride was redistilled twice in a stream of carbon dioxide. In every operation the apparatus used was constructed entirely of glass, with only a few well-ground connections.

The carbon dioxide was generated by the action of hydrochloric acid on white marble. The gas was passed through a large tower containing beads coated with moist sodium bicarbonate, then through a similar tower charged with moist silver carbonate. Several wash-bottles containing glass beads and concentrated sulfuric acid served to dry the gas sufficiently for the purpose. In order to remove any possible traces of acid it was finally conducted over fused, granulated potassium carbonate.

Ordinary distilled water was used in washing the columbium hydroxide. The water used in the subsequent operations had been distilled from alkaline potassium permanganate, then from a small quantity of acid potassium sulphate; the product was redistilled as needed.

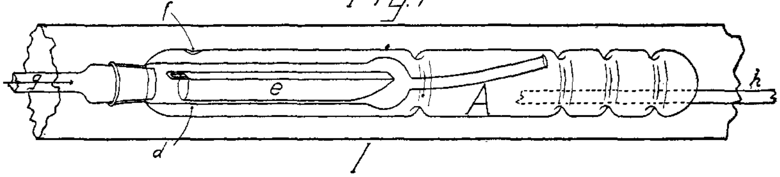
The method proposed for the determination of the ratio consisted essentially in heating the dehydrated metacolumbate in the vapor of sulfur monochloride; columbium was expelled as chloride or oxychloride, while sodium chloride remained behind. Since the air could not be removed completely from the apparatus by the sulfur monochloride alone, carbon dioxide was used for this purpose, serving, at the same time, as a vehicle for the former.

It was soon found that the columbium could not be expelled completely from the columbate, even by a prolonged action of the sulfur monochloride. The residue would finally come to constant weight, it is true, but numerous trials showed that a portion (amounting to several per cent.) of the columbate always remained unaffected, even when the salt had been ground to a fine powder. However, when the residue in the boat was moistened with water, evaporated to dryness, and again subjected to the action of sulfur monochloride a fresh sublimate of the chloride of columbium would appear.

In this manner the reaction could finally be carried to completion; that is to say, the residue would eventually consist of pure sodium chloride and completely dissolve in water. This seemed to indicate that the difficulty was merely mechanical in nature. At first it was thought that the sodium chloride formed was possibly raised to incipient fusion by the heat of the reaction, and that it thus protected part of the columbate from further action. The true explanation of this difficulty, however, is probably to be sought partly in the molecular magnitude of sulfur monochloride, by virtue of which it diffuses through a porous mass more slowly than, let us say, hydrogen; partly in the fact that sodium chloride has a lower density, in other words, is more voluminous, than sodium columbate and thus may protect the unchanged columbate in the interior of a particle much more effectively than if the respective densities were interchanged. Possibly the carbon dioxide also had a retarding influence. However this may be, evaporation with water proved to be indispensable and gave results which, for completeness, left nothing to be desired.

Evidently an ordinary boat was unsuitable for this treatment and for the evaporation with water. Several devices were tried; they need not be described here, with the exception of the one finally adopted. It gave entire satisfaction, and is shown in Fig. 1.

Fig. 1



The reaction tube (A) consisted of fused, transparent quartz; it was about 150 mm. long and 18 mm. in diameter. The quartz tube (*g*) was not ground into (A), but merely formed a smooth contact joint. The inner tube (*d*) was wide enough to admit a long, narrow platinum boat (*e*) having convex sides conforming to the tube, so as to increase the capacity. The exit from the reaction tube is indicated at (*f*), a small circular opening. The columbate, roughly dehydrated in a current of dry air, was put into the boat (*e*) and the dehydration completed in this apparatus. Carbon dioxide was removed from all air used in drying; this precaution, however, was probably superfluous. The quartz reaction tube was never heated directly. It was supported by a rack made of stout "nichrome" ribbon covered with platinum foil and placed in another quartz tube (I) to which the heat was applied. The temperature was raised gradually until it finally reached 760–800°; it was measured by means of a thermocouple, part of which is indicated at (*h*). Although the columbate was infusible, the crystals directly in contact with quartz had a slight corroding action on the latter at elevated temperatures; for this reason the platinum boat was used in the dehydration. During the entire operation a steady stream of dry air entered the tube through (*g*). It has been said before that the salt gives up the bulk of its water of crystallization at a rather low temperature; for the expulsion of the last traces of water, however, a temperature of nearly 800° was found to be necessary. The complete dehydration required at least ten hours of continued heating, usually much longer. It may be stated that the completely dehydrated columbate was remarkably stable toward further ignition. In one instance the perfectly dry salt was ignited again for about ten hours, in the manner indicated; it varied less than 0.02 mg. from the original weight.

In each determination the columbate was dehydrated in this manner until its weight remained practically constant. When this had been accomplished the granular residue ($NaCbO_3$) was allowed to glide from the platinum boat into the lower compartment of the quartz tube and the boat withdrawn; the exact weight of the columbate was then determined, hence the weight of the boat did not figure in the calculation. The substance was now ready to be acted upon by sulfur monochloride.

The apparatus used for the decomposition of the columbate by sulfur monochloride is sketched in Figs. 2 and 3, with the exception of the carbon dioxide generator and the drying train. It was constructed entirely of glass. All ground connections had been fitted with great care as no lubricant could be used; they were held in position by wire clamps. The diagram needs little explanation. The apparatus could be disconnected by moving the distilling bulb (N) in the direction (*o,p*), thereby turning (*l*) about the vertical axis (*k,l*) and the neck of the distilling bulb slightly about its ground-in tube (*p*). The unit (*o,q,r*) could then be removed by turning about the axis (*o,r*). After the introduction of the quartz tube with the weighed anhydrous columbate into the combustion tube the air was displaced by dry carbon dioxide through (*s*) and (*t*). Sulfur monochloride was then driven into the tube by gently heating the distilling bulb and admitting carbon dioxide through (*u*), while (*s*) was turned off. Part of the sulfur monochloride condensed again in (*o,r*) and was driven by a gentle heat into the combustion tube as needed. The bulbs (*v,v,v*), were very useful in preventing liquid sulfur monochloride from reaching the reaction tube and causing spluttering. By this arrangement the flow, of the sulfur monochloride could be regulated at will. In the meantime a constant stream of carbon dioxide entered the combustion tube through (*t*), thus preventing the monochloride and other volatile products from "backing up" and reaching the ground joint at (*w*). The charge was just heated sufficiently to drive the volatile products of the reaction beyond the quartz tube; only a moderate heat was required. In spite of the gas "pocket" at (*x*) the reaction proceeded with ease. The connection at (*r*) was similar to the one described in the dehydrating apparatus.

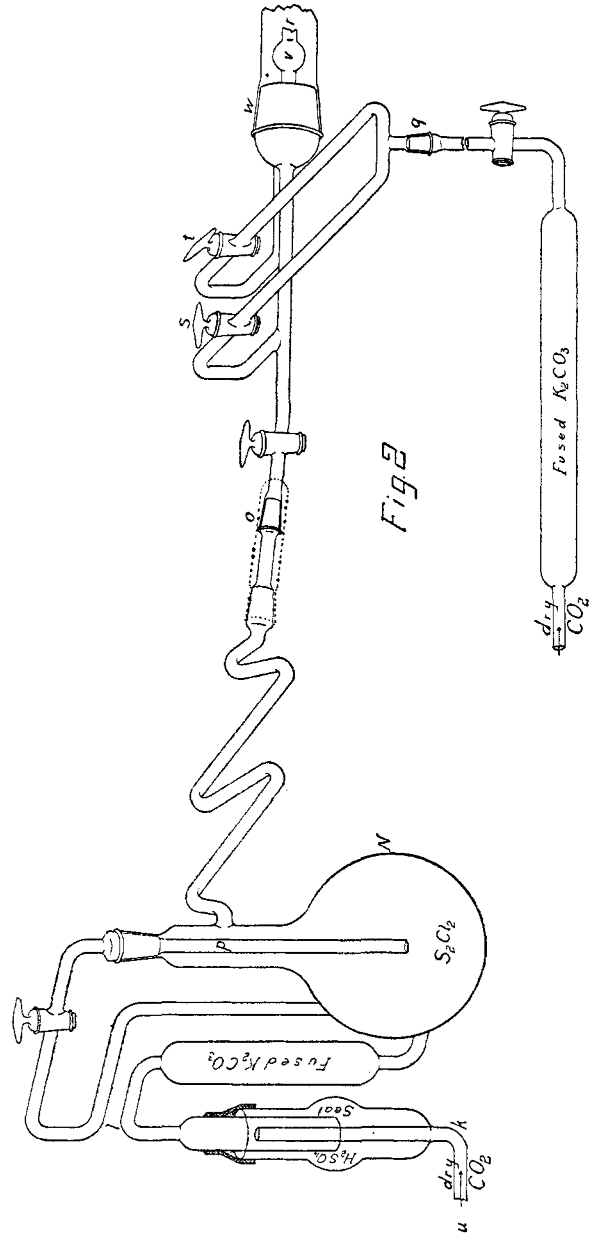


Fig. 2

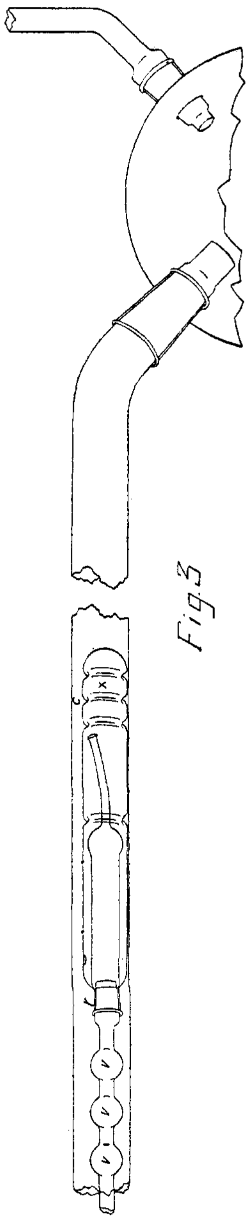


Fig. 3

When the reaction had become rather sluggish the supply of sulfur monochloride vapor was cut off, the excess of the latter removed by carbon dioxide, and the tube allowed to cool. The residue in the quartz tube was then covered with a little water containing a drop of pure hydrochloric acid, the tube placed in a suitable test-tube with a loose-fitting lid, the whole supported at an acute angle from the horizontal, and the liquid evaporated in an oven, at 110–120°. At this temperature no ebullition of the salt solution took place and, as several accurate weighings showed, no loss of sodium chloride was occasioned by such an evaporation.

The dry residue was then treated again with sulfur monochloride as before, and again evaporated with water. These operations were repeated until a perfectly clear solution of sodium chloride was obtained in the reaction tube on the addition of water. After that the dry residue was given one more treatment with the monochloride. In this manner the completeness of the reaction could be determined much better than by attempting to reach constancy in weight, for at this stage the sodium chloride retained varying traces of water that were not removed during the subsequent treatment with sulfur monochloride. In almost all cases four evaporations with water were sufficient. In these evaporations the sodium chloride "crept" (usually as far as the middle constriction) and thus exposed the unattacked residue. The lower end of the reaction tube was corrugated, as indicated in the sketch at (*c*), in order to help distribute the residue and to prevent it from forming a single compact mass; this construction facilitated the reaction considerably.

In some preliminary experiments the quartz tube became slightly etched, particularly when a fairly high heat had been applied to the combustion tube. This was probably due to the action of the finely divided columbate remaining after an evaporation with water. In the final determinations only a gentle heat was applied and the difficulty was entirely overcome, for the tube showed practically no variation in weight. It was also noticed that the presence of the hydrochloric acid in the water minimized this action upon the quartz.

As sulfur dioxide is probably produced in the sulfur monochloride reaction it was to be feared that the residual sodium chloride might be contaminated by sulfite or possibly, in the presence of a trace of air, by sulfate. As a matter of fact, an extremely slight test for sulfuric (or sulfurous) acid was obtained in two preliminary experiments. It was probably due to a trace of air in the apparatus; numerous trials convinced the writers that sulfites (or sulfates) are not normally produced in this reaction. Nevertheless a careful test for sulfuric acid was carried out after the completion of each determination. None was found in the final experiments. This test was made as follows: To the residual sodium chloride, dissolved in water, a drop of hydrochloric acid and a little bromine water are added. The solution was heated to boiling and tested with barium chloride; it was allowed to stand for at least twelve hours. It may be added that the hydrochloric acid present in the water before evaporation also would have served to destroy any sulfite.

When the reaction in sulfur monochloride had come to an end the sodium chloride had to be dried for the final weighing. This was done by heating the salt, very gently at first, in a current of dry air. The apparatus already described under the dehydration of the columbate was used for this purpose (see Fig. 1). The temperature was raised gradually to the fusion point of sodium chloride; during this operation the mouth of the quartz tube was kept much cooler than the rest. In this manner no volatilization of salt from the tube took place. At least two or three weighings were made until the weight of the sodium chloride had become practically constant.

During the weighings the quartz tube was enclosed in a glass-stoppered tube made of light test-tube glass. In each case the weight was obtained by comparing the apparatus containing the substance, by substitution, with a counterpoise which was an exact duplicate of the former. The two weighing bottles containing the quartz tubes were allowed to cool in a large desiccator and were stoppered under the same atmospheric conditions, just before weighing. A No. 10 Troemner balance was used; it was easily sensitive to 0.02 mg. The weights had been carefully calibrated by the substitution method.

All weighings were reduced to the vacuum standard. The density of the ignited sodium columbate was determined in water and found to be 4.19; that of sodium chloride was assumed to be 2.14; the density of the weights was 8.4. The other constants used are: Cl = 35.46; Na = 23.00; O = 16.00. The results are given in Table I.

TABLE I.—ATOMIC WEIGHT OF COLUMBIUM.

Number of analysis.	(*a*) Weight of anhydrous $NaCbO_3$ in vacuum. Grams.	(*b*) Weight of NaCl in vacuum. Gram.	Ratio *a* : *b*.	Atomic weight of *Cb*.
1	0.36419	0.12975	2.80686	93.089
2	0.69113	0.24617	2.80753	93.128
3	1.04904	0.37368	2.80732	93.116
4	1.64337	0.58516	2.80841	93.180
5	1.33367	0.47487	2.80849	93.185
6	0.88051	0.31366	2.80721	93.110
7	1.29947	0.46289	2.80730	93.115
			Average,	93.13

In analyses 6 and 7 a recrystallized sample of sodium columbate was used which had been prepared from Chapin's double fluoride and pure sodium hydroxide (Hermann's method; see Section I). In view of the fact that this salt had been prepared by a different method from a different preparation the two results seem to agree tolerably well with the average of the first five. In considering the variation in the series it must be borne in mind that samples 1 to 5 had not been recrystallized on account of the difficulties previously explained; as the columbate tends to hydrolyze in water solution, apparently little is to be gained even by a recrystallization. Although this circumstance may be pointed out as a weakness of the method, it should be borne in mind that practically all columbium derivatives suffer from similar or even more serious defects.

Summary.

(1) The relation existing between the 7:6 and 1:1 sodium columbates has been established; they have been shown to be mutually convertible, and both have been prepared by new methods. Characteristic differences between these salts have been pointed out.

(2) Sulfur monochloride has been used, for the first time, directly for the determination of an atomic ratio; its applicability has been demonstrated. The method and the apparatus devised may be of value in other work.

(3) The atomic weight of columbium, as obtained from the ratio $NaCbO_3$: NaCl, was found to be 93.13. Although this figure is considerably lower than the present international value, 93.50, it is hoped that the former will prove more reliable than those recorded heretofore.

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THE EXTRACTION AND SEPARATION OF THE RADIOACTIVE CONSTITUENTS OF CARNOTITE.

BY H. M. PLUM.

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Ever since the discovery of radium by Mme. Curie and the announcements of its wonderful properties, there has been a very great demand for this element. On account of its scientific interest, such extensive investigations have been carried out that the supply of radium at all times has fallen short of the demand. The more recent claim that it has therapeutic value in the treatment of such diseases as cancer has so greatly increased the demand, that the study of the radium-producing ores, along with the best methods of extracting the radioactive material, has become extremely important. In view of these facts it can readily be seen that the demand for radium will be on the increase, and that any research which would point out efficient and practical methods for the recovery of this element will be of both scientific and practical value.

This paper presents the results of a critical investigation, carried out under the direction of Dr. Herbert N. McCoy, of various methods of