

ART. XLVIII.—*The Quantitative Determination of Rubidium by the Spectroscope*; by F. A. GOOCH and J. I. PHINNEY.

[Contributions from the Kent Chemical Laboratory of Yale College—XVIII.]

IN a recent paper issued from this laboratory\* the possibility of determining small amounts of potassium quantitatively by means of the flame spectrum was demonstrated. The work which we are about to describe was performed in the endeavor to see how far similar methods might be applicable to the quantitative determination of rubidium. It was shown in the former work that hollow coils of platinum wire may be adjusted to hold definite amounts of liquid and that, by taking care to plunge the coil while hot into the liquid and to remove it from the liquid with its axis inclined obliquely to the surface, it is possible to take up constant amounts through a long series of experiments. It thus becomes possible to bring definite amounts of any soluble substance into a flame to be viewed spectroscopically. The potassium salt best adapted to spectroscopic use proved to be the chloride, and it was found to be advantageous to dry the coils over a hot radiator before introducing them into the flame. A large Muencke burner gave the best sort of flame, an ordinary single prism spectroscope provided with an adjustable slit (the width of which we were able to fix by closing it upon wires of known diameter) and an observing telescope moveable so that different portions of the spectrum might be shut out at will, served sufficiently well for the work. The coils were made of No. 28 platinum wire (0.32<sup>mm</sup> in diameter) wound in about thirty turns to a spiral 1<sup>cm</sup> long by 2<sup>mm</sup> in diameter and twisted together at the ends to form a long handle. With the apparatus described it was found possible, under the most favorable conditions, to recognize the characteristic red line of the potassium spectrum when only  $\frac{1}{1000}$  mg. of potassium, in the form of the chloride, was brought to the flame. It appeared, furthermore, that a comparison of the brightness of two spectra produced in close succession could be made with all the accuracy to be anticipated in photometric measurements, and that therefore by gradual dilutions and successive testings a solution of potassium chloride of unknown strength could be brought to the point of containing as much potassium to the coil-full (and so, of course, to the cubic centimeter or any other chosen volume) as a standard solution of known strength. By noting the final

\* Gooch and Hart; this Journal, xlii, p. 448.

volume to which such an unknown solution was brought in the process of equalizing its spectrum with that of the standard its total contents in potassium was determined. In this manner the strength of solutions of pure potassium chloride proved determinable with accuracy, but when the effect of intermixing pure sodium chloride with the potassium salt was studied it transpired that the brilliance of the potassium spectrum was markedly increased by the presence of the sodium in the flame, the maximum increase, which amounted to twenty per cent, appearing when the ratio of sodium chloride to potassium reached 100 : 1. It was found, however, that the practical difficulty of determining potassium in presence of sodium could be largely overcome by taking the precaution to bring the test solution and the standard to apparent equality as regards the potassium line, then to bring the solutions to an equality in respect to the sodium line by addition of sodium chloride to the standard, and finally to readjust the volumes of test and standard until the potassium lines were again equal. The accuracy of the determination of the potassium is, however, in spite of the precaution, somewhat affected by the presence of sodium,—the error, though, sometimes falling as low as  $\frac{1}{10}$  mg. in 10 mg., rising occasionally to 1 mg. in 15 mg. With the excellent gravimetric method which we possess for the determination of potassium recourse would, naturally, never be taken to the spectroscopic method except in cases when the determination of small absolute amounts are concerned, but in such cases the spectroscopic method may prove a convenience.

In the work upon potassium the observations of the red line were made in the ordinary laboratory in diffused light, but preliminary experimentation upon the rubidium spectrum immediately developed the fact that the blue lines are better to work by in the case of this element, and that a dark room becomes a necessity. For the experiments to be described pure rubidium chloride was prepared by many fractional precipitations by alcohol out of aqueous solutions, and in settling the question as to the coils which should be used the choice fell upon the size holding 0.02 grm. of water and made of the No. 28 wire, the superior stiffness of these and consequent constancy in capacity giving them the advantage over smaller coils of finer wire, though the latter are capable of bringing out greater sensitiveness of the reaction. We found, for example, that under the most favorable conditions as to height of flame and width of slit, 0.0002 mg. of rubidium chloride produced the blue lines at the last limit of visibility when the larger and heavier coil was in the flame; with a coil holding 0.006 grm. of water and made of very fine wire the more

immediate volatilization of the chloride so increased the delicacy of the spectroscopic reaction that it was possible to see the lines from 0.00005 mg. of the salt. These figures serve as an indication of the possible delicacy of this method of producing spectra, but it should be remembered that all eyes do not see the rubidium lines with equal ease.

In experimenting with rubidium sulphate in place of the chloride the lighter coil appeared to lose its advantage in point of delicacy of the indication over the larger coil, possibly because the amount of metal introduced into the flame has less influence upon the rate of vaporization of the less volatile sulphate, and the lines of the sulphate appeared equally distinct and of longer duration than those of the chloride; but, while we judged the sulphate to be rather preferable in qualitative work, our earlier preliminary quantitative experiments led us to abandon it for the purposes of our investigation on account of the great uniformity in the lines yielded by the chloride. We found it desirable in comparative tests of brightness to employ as the standard the lines given by amounts of the chloride not exceeding 0.0005 mg. to 0.0007 mg., to set the slit at a width of 0.2<sup>mm</sup>, and to bring the coils to the flame in sets of three—the first, usually a standard, serving to fix the position of the lines so that the comparative distinctness of the lines given by the other two might be the more readily determined. The tables below contain the record of an attempt to dilute a solution of the pure chloride to the strength of the standard solution under the guidance of comparative tests of the brilliance of the spectral lines yielded by the residue left upon the wires after the evaporation of the solutions taken up by coils of equivalent capacity. Dilutions were made in ordinary graduated cylinders of suitable capacity.

EXPERIMENT I.		
Standard. Rubidium in a coil-full ( $\frac{1}{16}$ cm <sup>3</sup> ).	Test (known to contain 10 mg Rb.). Volume in cm <sup>3</sup> .	Line of test compared with standard.
0.0005 mg.	200	Brighter.
" "	300	Brighter.
" "	350	Brighter.
" "	370	Brighter.
" "	390	Brighter.
" "	400	{ Brighter (faintly). Brighter (faintly). Doubtful.
" "	400	
" "	400	
" "	410	{ Brighter (faintly). Weaker.
" "	410	
" "	420	{ Equally bright. Weaker.
" "	420	
" "	430	Invisible.

When the volume of the test-solution reaches 400 cm<sup>3</sup> the indications are, on the whole, that the solution is still stronger than an equal volume of the standard; and when the volume amounts to 420 cm<sup>3</sup> it is safe to conclude from the indications that the test-solution is the weaker. If the mean of the numbers representing these two volumes be taken as probably indicative of the volume at which the test and standard lines are at an equality we have the estimated amount of rubidium in the test-solution given by multiplying the volume in cubic centimeters by the number of coil-fulls in 1 cm<sup>3</sup> and the product by the amount of rubidium contained in a coil-full of the standard solution— $410 \times 50 \times 0.0005 = 10.25$  mg. The amount of rubidium actually taken in the test-solution was 10 mg., and the error of the mean value assumed is 2.5 per cent+, between extremes corresponding to an error of 0 and 5 per cent +, respectively.

EXPERIMENT II.

Standard. Rubidium in a coil-full ( $\frac{1}{80}$ cm <sup>3</sup> ).	Test (known to contain 10 mg. Rb.). Volume in cm <sup>3</sup> .	Line of test compared with standard.
0.0005 mg.	340	Brighter.
" "	370	{ Equally bright.
" "	370	
" "	390	{ Weaker.
" "	390	

$$\text{Found } \frac{370 + 390}{2} \times 50 \times 0.0005 = 9.5 \text{ mg.}$$

$$\text{Taken } \dots\dots\dots 10.0 \text{ "}$$

$$\text{Error } \dots\dots\dots 0.5 \text{ " } = 5 \text{ per cent.}$$

EXPERIMENT III.

Standard. Rubidium in a coil-full ( $\frac{1}{80}$ cm <sup>3</sup> ).	Test (known to contain 10 mg. Rb.). Volume in cm <sup>3</sup> .	Line of test compared with standard.
0.0005 mg.	300	Brighter.
" "	360	Equally bright.
" "	380	Brighter.
" "	380	Brighter.
" "	390	Brighter.
" "	400	Weaker.
" "	410	Weaker.

$$\text{Found } \frac{390 + 400}{2} \times 50 \times 0.0005 = 9.875$$

$$\text{Taken } \dots\dots\dots 10.$$

$$\text{Error } \dots\dots\dots 0.125 = 1.25 \text{ per cent.}$$

These results make it plain that when the comparison is made between solutions of pure rubidium chloride the spectroscopic method is capable of yielding fair approximations to truth. In the practical determination of rubidium, however, the question of the effect of the presence of sodium and potassium which naturally accompany it is of importance. Attention was therefore turned next to the consideration of this point, and the record of observations as to the influence of sodium upon the brightness of the rubidium spectrum is contained in the accompanying tabular statement.

Standard. Rubidium in a coil- full ( $\frac{1}{32}$ cm <sup>3</sup> ).	Test solution. Sodium in a coil-full.	Comparison of lines of test by pairs.	Comparison of lines of test with standard.
0.00066 mg.	{ 0.00026 mg. 0.00260 " }	{ Slightly brighter. Slightly fainter. }	{ Brighter.
" "	{ 0.00130 " 0.00260 " }	{ Equally bright.	{ Brighter.
" "	{ 0.00260 " 0.00520 " }	{ Equally bright.	{ Brighter.
" "	{ 0.00260 " 0.00660 " }	{ Brighter. Fainter. }	{ Brighter.
" "	{ 0.00260 " 0.00780 " }	{ Brighter. Fainter. }	{ Brighter.
" "	{ 0.00260 " 0.01500 " }	{ Brighter. Invisible on account of glare.	{ Brighter. Invisible.

It appears that within limits the presence of sodium in the flame increases the brilliance of the rubidium spectrum. The brightness of the lines is raised under the conditions to a maximum by the presence of sodium to forty per cent of the weight of the rubidium, and increase in the amount of sodium does not further influence the brightness of the lines until the proportion of sodium to rubidium is as ten to one; or, speaking broadly, the difference between the dissociating effect of sodium upon the rubidium chloride (to which we attribute the effect noted) does not appear to be materially different whether one or a score of molecules of sodium chloride are present to one of the rubidium chloride. But when the proportion of sodium to rubidium much exceeds ten to one the glare of light diffused through the entire spectrum (though the sodium line itself may be cut off) begins to affect the vision, and as the increase advances ultimately extinguishes the rubidium lines utterly. The degree of increase in brilliance when the lines are at a maximum was determined by diluting the test-solution until a coil-full gave a line equally brilliant with that of the standard.

Standard. Rubidium in a coil-full ( $\frac{1}{8}$ cm <sup>3</sup> ).	Test solution. Rubidium in a coil-full with $\frac{1}{10}$ of its weight of sodium.	Line of test compared with standard.
0.00066 mg.	0.00066 mg.	Brighter.
" "	0.00048 "	Brighter.
" "	0.00046 "	Brighter.
" "	0.00044 "	Equally bright.

It is plain that at the maximum degree of brilliance the sodium is responsible for an increase of fifty per cent in the brightness of the lines.

The details of similar experiments in which potassium chloride was introduced into the flame with the pure rubidium chloride are given in the accompanying tabular statement.

Standard. Rubidium in a coil-full ( $\frac{1}{8}$ cm <sup>3</sup> ).	Test solution. Potassium in a coil-full.	Comparison of lines of test taken by pairs.	Comparison of lines of test with standard.
0.00066 mg.	0.00020 mg.	Slightly fainter.	Brighter.
	0.00040 "	Slightly brighter.	
	0.00020 "	Fainter.	Brighter.
	0.00340 "	Brighter.	
	0.00040 "	Equally bright.	Brighter.
	0.00066 "		
0.00066 mg.	0.00040 "	Brighter.	Brighter.
	0.00340 "	Fainter.	
	0.00066 "	Equally bright.	Brighter.
	0.00132 "		
	0.00066 "	Brighter.	Brighter.
	0.00246 "	Fainter.	
	0.00066 "	Brighter.	Brighter.
	0.00660 "	Fainter.	
	0.00066 "	Brighter.	Brighter.
	0.01320 "	Fainter.	
	0.00066 "	Brighter.	Brighter.
	0.02000 "	Fainter.	
	0.00066 "	Brighter.	Brighter.
	0.02660 "	Fainter.	
	0.00066 "	Brighter.	Brighter.
	0.03340 "	Fainter.	
	0.00066 "	Brighter.	Brighter.
	0.03340 "	Invisible.	

From these results it appears that the presence of potassium produces an effect upon the rubidium lines similar to that of sodium; and, furthermore, the addition of 0.0004 mg. of potassium in the form of chloride to 0.00066 mg. of rubidium also in the form of chloride brings out the maximum brightness which is not materially changed by further addition of

potassium up to about 0.0013 mg., but that the increase of the potassium to 0.0034 mg. results in diminution of brightness. In other words, it seems that a single molecule of potassium chloride has approximately the same dissociating effect upon the molecule of rubidium chloride in the flame as that brought about by a greater number, that the presence of potassium in the proportion of five parts to one of the rubidium begins to influence visibility unfavorably, that when this proportion rises to thirty to one of the elements (or twenty to one of the chlorides) the lines appear about as distinctly as if no potassium were present, and that an increase of proportion to fifty to one may bring about a sufficient glare of light to reduce the rubidium lines to invisibility. The degree of increase in brilliance due to the action of potassium when that element is present in proportions suitable to induce the maximum effect is shown in the following record.

Standard. Rubidium in a coil-full ( $\frac{1}{16}$ cm <sup>3</sup> ).	Test solution. Rubidium in a coil-full with its own weight of potassium.	Line of test compared with standard.
0.00066 mg.	0.00066 mg.	Brighter.
" "	0.00064 "	Brighter.
" "	0.00057 "	Brighter.
" "	0.00049 "	Brighter.
" "	0.00044 "	Equally bright.
" "	0.00040 "	Fainter.

It appears that the presence of 0.00044 mg. of potassium is capable of increasing the brilliance of the lines yielded by 0.00044 mg. of rubidium to an equality with the lines given by 0.00066 mg. of the pure salt; or, that the maximum increase of brightness amounts to fifty per cent.

It is evident, therefore, that means must be found to effect the separation of the rubidium from sodium and potassium, or of bringing test and standard to the same condition as regards the presence of these elements, before any reasonable degree of accuracy can be expected in the spectroscopic determination of rubidium as it ordinarily occurs in nature. The separation from sodium is easily accomplished by the conversion of the salts to the form of chloroplatinates; but for the quantitative separation of rubidium from potassium there is no good method known. The question as to the practical value of the spectroscopic reaction of rubidium for purposes of approximate quantitative analysis resolves itself into the problem as to whether by matching potassium lines as well as the rubidium lines (following the method outlined in the determination of potassium in presence of sodium), and so bringing the lines of test and standard equally under the influence of potas-

sium, it is possible to make the comparison between the rubidium lines trustworthy. It was shown in the former paper that in matching solutions of potassium by means of the red line there is no difficulty; but the convenience of being able to use the spectroscope without readjustment throughout the entire experiment made it desirable to see whether the blue line of potassium might not serve sufficiently well in the comparison. It is hardly necessary to reproduce here in detail the evidence bearing upon this point, but we found as the result that the potassium may be determined by the use of the blue line with an error amounting to 10 per cent or 20 per cent, which, though far greater than that inherent in the use of the red line, admits of the attainment of determinations which should be accurate enough for the present purpose. We proceeded, therefore, to make a determination of rubidium in presence of potassium by the process referred to, the details of which are given in Experiment IV.

EXPERIMENT IV.

Standard solution containing  $\left. \begin{array}{l} 0.0005 \text{ mg. Rubidium} \\ 0.0015 \text{ " Potassium} \end{array} \right\}$  to the coil-full.

Test solution contained 8 mg. rubidium and no potassium.

Step 1.	Step 2.	Step 3.	Step 4.	Step 5.
Preliminary				
Preliminary test for Rb.	matching of K line.	Rematching of Rb line.	Readjustment of K line.	Final matching of Rb line.
Test at 20 cm <sup>3</sup> gave Rb line like standard.	Test at 20 cm <sup>3</sup> gave K line like standard when 1 mg. of K had been added.	Test at 35 cm <sup>3</sup> gave Rb lines like standard.	Test at 35 cm <sup>3</sup> gave K line like standard when 2 mg. were present.	Test at 35 cm <sup>3</sup> gave Rb line like standard.

Rubidium found  $35 \times 50 \times 0.0005 = 0.875$  mg.

“ taken ..... = 0.8 “

Error ..... = 0.075 “ = 9.4 per cent.

It is evident that the percentage error is considerable, but inasmuch as the application of the process would naturally be to the determination of small absolute amounts of rubidium we thought it desirable to go a step further to see whether means are at hand for separating large amounts of potassium from small amounts of rubidium with an approach sufficiently near to completeness to bring the potassium present within the limits allowed by the spectroscopic method. After some experimentation we fixed upon the simplest possible procedure, viz: the solution of the salts in the least possible amount of water, precipitation of the mass of potassium chloride by addition of alcohol, filtration, and the evaporation of the filtrate.



In Experiments V, VI, VII, this mode of working was put to the proof. The amounts of rubidium indicated were dissolved in the form of the chloride in water, 0.1 gm. of potassium chloride was added, and the solution was evaporated and treated as described.

	Rubidium taken in the form of chloride.	Potassium taken in the form of chloride.	Rubidium found.	Absolute error.	Percentage error.
V.	1 mg.	0.1 gm.	0.8 mg.	0.2 mg.	20 per cent.
VI.	2 “	0.1 “	1.7 “	0.3 “	15 per cent.
VII.	1 “	0.1 “	0.9 “	0.1 “	10 per cent.

The error of the process is manifestly large, and only roughly approximate results can be hoped for when large amounts of rubidium are dealt with; but, if the question is the estimation of only a few milligrams of rubidium, it will appear, we think, in view of the fact that the only alternative is an indirect process, that even this great error is not absolutely prohibitive of what may be called fair determinations.