A SIMPLE PROCEDURE OF SEMI-QUANTITATIVE SPECTRAL ANALYSIS OF CALCIUM, STRONTIUM, BARIUM AND LITHIUM.

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In the course of a research on the permeability of the frog-skin, it occurred to me to analyse very dilute solutions of alkali and alkali-earth metals. In this case, I applied the spectral analysis introducing some improvements in its practical procedure, which enabled me to perform the semi-quantitative analysis, and the results thus obtained were accurate enough for the purpose of biochemical studies. On account of the simplicity of the method, which may be carried out even in a laboratory not equipped with modern spectroscopical instruments, I believe, it is worth describing.

Apparatus Employed. An induction coil which can discharge through the maximum spark gap of 3.5 cm. is connected to a fulgurator, the positive pole of which comes from the bottom of the vessel containing the solution to be tested, and its point protrudes slightly above the liquid surface. The distance between the poles is adjusted to be 1–2 mm., whichever gives the best result. In the primary circuit of the induction coil stands a battery, as well as a reversing key (Fig. 1).

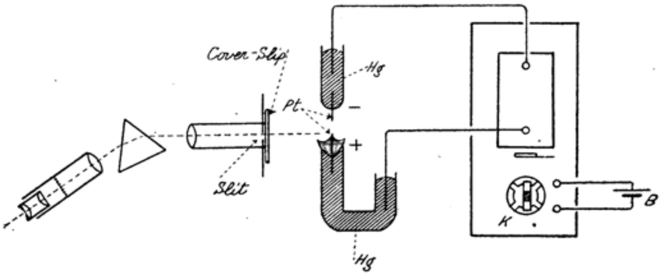

Fig. 1.

By this arrangement, in which the poles are reversed(1) to the usually adopted system, the spark is highly luminous at the anode and the spectral

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(1) This process differs from the well-known "procédé du spectre de renversement" after Lecoq de Boisbaudran in the respect, that in that classical method the solution itself serves as the anode, and it is the luminesced part of the solution that is observed spectroscopically.

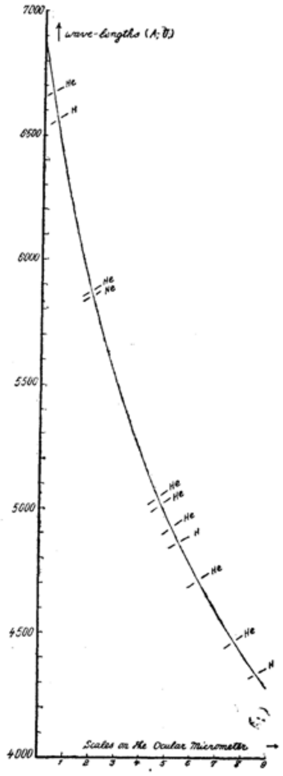

Fig. 2.

lines thus observed, in directing carefully the collimator of the spectroscope towards the point of the anode, are quite specific to the metal in the solution, accompanied by a number of non-specific lines. The spectroscope employed was an ordinary prism spectroscope of low dispersion, D_1 and D_2 lines of sodium being just possibly resolved.

The Determination of the Wave-lengths. As the standards of the wave-lengths of spectral lines, some neon-, helium- and hydrogen- lines were used; these spectral lines of known wave-lengths(1) were observed through an eye-piece provided with an ocular micrometer on its focal plane, in adjusting the direction of the telescope such that the yellow line of neon (5852.4 Å) comes just upon the scale division 2.00 (Fig. 2), and a curve which represents the relation between the wave-lengths (ordinates) and the micrometer scales (abscissae) was drawn. By the aid of the ocular micrometer and this reference curve, the wave-length of any unknown line is easily determined approximately.

As we are dealing with the spark spectrum across air between the platinum electrodes, it is expected that the lines due to air and platinum present themselves constantly as non-specific lines. Care must be taken, therefore, not to confuse them with those to be identified in the practise of analysis. The most marked of them are,

Colour	λ observed.	λ identified.(2)	Probable source
Green	5685	5686, –80	N
Green	5008	5001, –05,–07,–11	N
Blue	4862	4854	Pt
Blue	4712	4705, –10	O(?)
Blue	4660	4662	O(?)
Blue	4650	4642, –51 4643, –55	O(?) N
Blue	4484	4478	N

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(1) Baly, "Spectroscopy." 3rd ed., Vol. I, p. 126 (1924).

(2) Kayser, "Tabelle der Hauptlinien der Linienspectra aller Elemente," (1926).

Furthermore, in the fulgurator filled with a solution, there always appears a red line, $\lambda \doteq 6563$ due to hydrogen, even when filled with distilled water; and it is also quite difficult to suppress the appearance of the D-doublet lines, because of their very high sensibility.

For the determination of wave-lengths of those spectral lines that are situated in the red to yellow region, another simple method is applicable. The fulgurator, namely, is put close in front of the slit of the collimator, which is protected by a micro cover-slip from being soiled; and a neon lamp ("Glimlamp") stands behind the fulgurator. By such an arrangement any metallic line in this region, which is to be identified, may be found between two neon lines with known wave-lengths. We estimate by interpolation how far the line in question is located from one of the neon lines, say that having a shorter wave-length, and we can thus easily calculate the approximate wave-length of the metallic line.

In relation to this it may be worth remarking here that the "Glimlamp" gives 21 neon lines to the left of the yellow line ($\lambda=5852.4$)⁽¹⁾ inclusive, two of which—the one $\lambda=5364.9$ and the other probably composed of $\lambda=5606.4$ and $\lambda=5602.4$, but fused together owing to the low resolving power of our apparatus—are not found listed in some current text-books, while the line $\lambda=7032.4$ was not visible to the author.

Identification of the Specific Lines. By either of the two methods above mentioned, the wave-lengths of spectral lines of several metals produced by our reversed pole procedure are determined and thus identified, taking the Kayser's table⁽²⁾ or Eder and Valenta's atlas⁽³⁾ as reference. The results are given below:

LiCl, 1/750 M. Two lines are to be observed: an orange line is found between two neon lines, $\lambda=6143$ and $\lambda=6096$, while a red line is situated just resolvably close to the neon line $\lambda=6717$. Thus the estimated and identified wave-lengths of these red and orange lines are as follows:

Colour	λ estim.	λ ident.
Red	6712	6708
Orange	6101	6104

LiCl, 0.11 M. In this case also two and no more lines came to sight. They are, as identified by the reference curve,

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(1) Baly, loc. cit., p. 37 (1924).

(2) Kayser, loc. cit.

(3) Eder u. Valenta, "Atlas typischer Spectren," (1911).

Colour	λ estim.	λ ident.
Red	6715	6708
Orange	6100	6104

KCl, 1/750 M. No lines characteristic to this metal were observed, although persisting lines are expected at $\lambda = 4047$ and $\lambda = 4044$.

RbCl, 1/750 M. and *CsCl,* 1/750 M. In both cases, no specific lines bright enough to be utilised for our purpose, were detected.

$MgCl_2$, 1/750 M. Three lines of greenish blue colour were observed. They are so highly characteristic in their arrangement that we can recognise them at the first glance. The determination of their wave-lengths gave the following results.

Colour	λ estim.	λ ident.
Greenish blue	5177	5184.
„	5170	5173
„	5166	5167

$BaCl_2$, 1/750 M. The following six lines were observed:

Colour and intensity	Position compared with Ne-lines	
Red	Almost superposing on the line	6506.5
Bright orange	„	6143.0
Pale yellow	„	5852.4
Brilliant green		——
Brilliant blue		——
Brilliant indigo		——

Besides these lines, no bands were detected. The character of the barium spectrum obtained by this method shows thus more resemblance to its spark spectrum than to the flame spectrum.

$BaCl_2$, 0.09 M. In this concentration, barium chloride solution, if in a favourable condition, gives a number of distinct lines, the wave-lengths of which were determined as follows:

Colour	λ estim.	λ ident.
Red	6595	6595
"	6505	6499,–97
Orange	6137	6142
Striated in the orange region	6105	6111
	6060	6063
	6007	6019
	5993	5997
	5965	5972
Striated in the yellow region		
	5848	5854
	5828	5826
	5779	5778
Green	5537	5536
Blue	4935	4934
"	4920	4900,–03 (?)
Indigo	4556	4554

$SrCl_2$, 1/750 M. In this dilution, only few lines and bands were observed, namely two (sometimes more) weak green lines, two or more blue lines and one intense indigo line. Besides these lines, a striated red band and a distinct narrow orange band were visible.

$SrCl_2$, 0.1 M. The following numerous lines and bands were observed:

Colour and character	λ estim.	λ ident.
Red band	6880–6770	Band No. 1.
" "	6745–6640	" No. 2.
" "	6630–6555	" No. 3.
Red line	6460	6464,–66
Red band	6460–6420	Band No. 4.
Red line	6350	6346
Red band	6350–6310	Band No. 5.
Red line	6240	6229
Red band	6240–6207	Band No. 6.
" "	6105–6015	Band No. 7.
Orange-red line	6055	6059
Orange band	5975–5936	5970,–5940
Green line	5537	5543
" "	5518	5522
" "	5503	5504
" "	5476	5481
Blue line	5259	5259
" "	5237	5239
" "	5226	5230,–22
" "	4956	4962
" "	4871	4876,–72
" "	4831	4832
" "	4813	4812
" "	4793	4784
" "	4747	4742
" "	4723	4722
Indigo line	4612	4608
Violet line	—	4306
" "	—	4216

$CaCl_2$, 1/750 M. The following lines and bands were detectable:

Colour and character	Intensity
Orange-red line	Very weak, often invisible when the lamp is lighted.
Green line	
Red to orange band	Quite intense.
Narrow green band	

$CaCl_2$, 0.1 M. The wave-lengths of the following lines and bands were determined:

Colour and character	λ estim.	λ ident.
Red band	6525–6363	
Intense red band	6310–6157	
Lines in the intense red band	6250	6265
	6202	6202
	6180	6180
Orange line	5938	5933
Orange band	6155–5890	
Green band	5576–5493	
Lines in the green band	5559	5543
	5520	5517

Accuracy and Limit of Application of this Method. In order that this spectroscopical method may be utilised for the semi-quantitative analysis of certain metals from salt solutions, its accuracy should be determined beforehand with solutions containing the salts in various known dilutions. And it is recommended to list the results in reference tables characterising the arrangement and apparatus made use of by each worker. In the author's own case, it proved as shown in the following tables, in which the degrees of brightness of the lines and bands are marked with – (invisible), ± (hardly visible), + (visible), + + (bright) and + + + (brilliant). The results obtained with lithium, barium, strontium and calcium were satisfactory:

Colour and wave-length	Relative concentration (1 = 1/750 M.)					
	0.025	0.05	0.1	0.25	0.5	1
Lithium chloride:						
Red, 6708	–	±	+	+	+ +	+ +
Orange, 6104	–	–	±	+	+	+ +
Barium chloride:						
Red, 6499–7	–	–	–	–	+	+
Orange, 6142	–	–	±	+	+	+ +
Yellow, 5854	–	–	–	–	–	+
Green, 5536	–	–	+	+	+ +	+ + +
Blue, 4934	–	–	+	+	+ +	+ + +
Violet, 4554	–	–	–	–	+	+ +
Strontium chloride:						
Red bands	–	–	±	+	+	+ +
Orange band	–	–	–	±	+	+ +
Green lines	–	–	–	–	±	±
Blue lines	–	–	–	–	±	±
Indigo, 4608	–	–	±	+	+ +	+ + +
Violet, 4306	–	–	–	+	+ +	+ + +
Violet, 4216	–	–	–	+	+ +	+ + +

Colour and wave-length	Relative concentration (1=1/750 M.)					
	0.025	0.05	0.1	0.25	0.5	1
Calcium chloride:						
Intense red band	−	−	−	+	+	++
Orange band	−	−	±	+	+	++
Green band	−	−	−	±	+	+

The probable limits of detection of Ca, Sr and Ba by this method, calculated in terms of mg. of the metals in 1 c.c. of solution and compared with those of Bunsen's classical method as well as of Riesenfeld and Pützer's process, are shown below:

	Bunsen's flame analysis.	Riesenfeld & Pützer.	Present author.
Ca	0.2 mg in 1 c.c.	0.002	0.013
Sr	0.6 ”	0.03	0.029
Ba	14 ”	0.006	0.018
Li	—		0.0009

According to the description of Riesenfeld and Pfützer,(1) their method, which is often quoted as a process representing the highest sensibility attainable by the spectral analysis, requires at least about 1 c.c. of the solution to be tested, while in the present procedure, only 0.1 c.c. or even a smaller quantity of solution is sufficient to carry out one test, owing to the small capacity of the fulgurator-vessel.

Summary.

1. A simple procedure of the semi-quantitative spectral analysis has been described.

2. This procedure consists in observing salt solutions fulgurated in a special fulgurator, with the electrodes reversed, i. e. the anode in the solution.

3. Accuracy and limit of application of this method were carefully studied and it was found that this is especially suited for the analysis of minute quantities of lithium, calcium, strontium and barium.

In carrying out this study, the author owes much to the suggestion and encouragement of Prof. Hashida and Prof. Nagai, as well as to the kind interest and care taken by Prof. Y. Shibata of the Faculty of Science of this University. Sincere thanks are also expressed here to the friendship of Dr. Shinki of the Military Institute for Scientific Research.

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(1) Riesenfeld and Pfützer, *Ber.*, 46 (1913), 3140.