Quantitative Spectral Analysis. IX. Determination of Caesium by Emission-Spectra.

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I. **Introduction.** The chemical analysis of caesium contained in a sample solution, especially when caesium is contained in an insignificant amount, is exceedingly tedious in the process while less reliable in the outcome, principally owing to the difficulty of separating it from the other alkalies. The present writer has, nevertheless, tried to establish the definite method of quantitative analysis of caesium by means of emission-spectra.

II. **Sample Electrodes.** For the quantitative determination, the sample solution has been transformed into solid conductive electrodes in the following way: A sample solution of known or unknown caesium content and 20 c.c. of "sirupus simplex" of Jap. Ph. were mixed in a mortar. To this mixture 10 g. of carbon ("Nolit") were added and elaborately mixed and then heated in an air-oven for the express purpose of removing water contained in the mixture. When an appropriate consistency was thus obtained, it was moulded into tablets while hot, and they were further heated in an air-oven for further expelling any remaining volatile matter.

When the sample to be analysed was given in the form of solid substance, for example, such as ashes obtained from some plants or other, or some dry pulverized leaves, and stems of certain plants, or sometimes organic tissues of animals or insects, the sample was similarly rendered into the shape of tablets for sparking electrodes.

III. The Apparatus Used and the Method of Experiment. To excite sparks between a pair of electrodes, a transformer giving 10 kilovolts in the secondary circuit was used. Self-inductance of a magnitude of 5500 cm. was always inserted in the secondary circuit, but no capacity was inserted. The light emanating from an uncondensed spark between the electrodes was focussed by means of a lens on a slit of a constant deviation spectrograph. The dispersion of the spectrograph was 25 Å per mm. at $\lambda = 4560$ Å. The caesium lines at $\lambda = 4555.3$ and 4593.2 Å were detected, the former being more sensitive.

The method of analysis was consisted in drawing a density-concentration curve in connection with the line at 4555.3 Å so as to determine graphically the concentration of caesium chloride from the density of the caesium line in the spectrogram of an unknown sample. The so-called "method of comparison" was also tried, and both results were compared.

IV. The Sensitivity of the Spectrographic Analysis. The sensitivity of the spectrographic analysis of caesium chloride contained in the sample electrodes composed of carbon and "sirupus simplex" was determined in the same way as was already described.(1)

The relation between the percentage composition of caesium chloride in the electrodes and the intensity of the caesium line at $\lambda =$ 4555.3 Å is shown in Table 1 and Fig. 1, where d representing the galvanometer deflection measuring the density of the line. The sensitivity was thus graphically found to be 2×10^{-4}% under the conditions of the experiment. (See Fig. 3, a and b.)

Table 1.

CsCl (%)	d (mm.) $\lambda = 4555.3$ Å
5×10^{-4}	3.2
15×10^{-4}	9.9
3.0×10^{-3}	17.6
5.0×10^{-3}	28.2

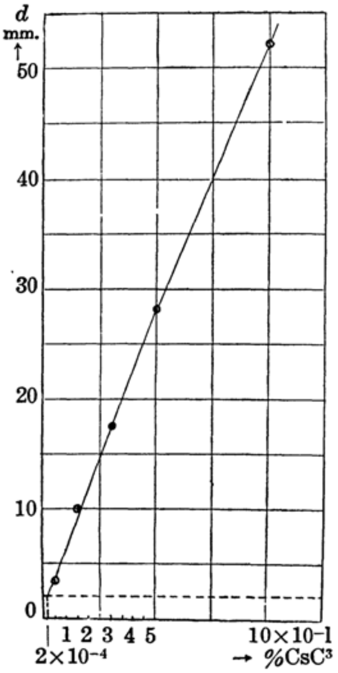

Fig. 1.

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(1) *Mem. Coll. Sci., Kyoto Imp. Univ.*, A, **14** (1931), 51.

The sensitivity tried by means of employing the electrodes composed of zinc oxide and hydrochloric acid was found to be too low. The cause of this lower sensitivity shown in the electrodes cemented with zinc oxide can be understood when we compare the ionization potential of caesium with those of zinc, carbon, etc., as indicated in Table 2.

Table 2.

Elements	Cs	Zn	Mg	Ca	C	Na	Rb	K
1st ioniz. potential (volts)	8.88	9.35	7.61	6.09	11.24	5.12	4.16	4.32

V. **Examples of Analysis.** The results of analysing a sample by the graphical method of applying the density-percentage composition relation is shown in Table 3 and Fig. 2, the microphotometer records being given in Fig. 3, c and d.

Table 3.

CsCl (%)	d (mm.) $\lambda = 4555.3$ Å
x	3.3
3×10^{-3}	7.2
6×10^{-3}	11.5
1×10^{-2}	19.2
1.5×10^{-2}	19.0
2×10^{-2}	33.7

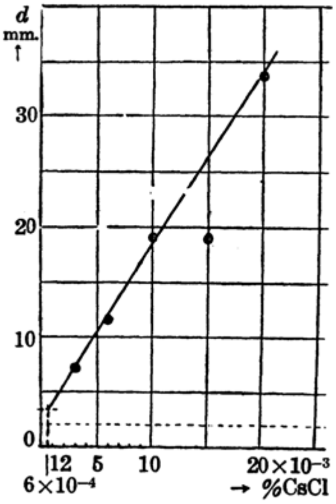


Fig. 2.

$x = 0.0006\%$ against the calculated value of 0.0005%.

The results of experiment showing how the method of comparison may be employed for the analysis of the same sample mentioned above, turned out to be as follows (see Fig. 4, a):

Let S denote the concentration of caesium chloride in the sample taken.

Ex. 1. $S = 0.0005\%$ CsCl.

CsCl (%)	d (mm.) $\lambda = 4555.3$ Å
0.0002	3.1
	4.9
S	8.0
	4.3
0.0008	12.3

By proportion we get,

$$6\times\frac{4.9}{9.2} = 3.2.$$

$$\therefore\ S = 0.0002+0.00032 = 0.00052.$$

$$\varDelta = 100\times\frac{2}{50} = 4.0\%.$$

Ex. 2. $S = 0.0030\%$.

CsCl %)	d (mm.) $\lambda = 4555.3$ Å
0.0020	10.7
	7.3
S	18.0
	16.1
0.0050	34.1

By proportion we get,

$$30\times\frac{7.3}{23.4} = 9.$$

$$\therefore\ S = 0.0020+0.0009 = 0.0029.$$

$$\varDelta = 100\times\frac{1}{30} = 3.3\%$$

Such a high order of accuracy can hardly be attained by any chemical method of analysis.

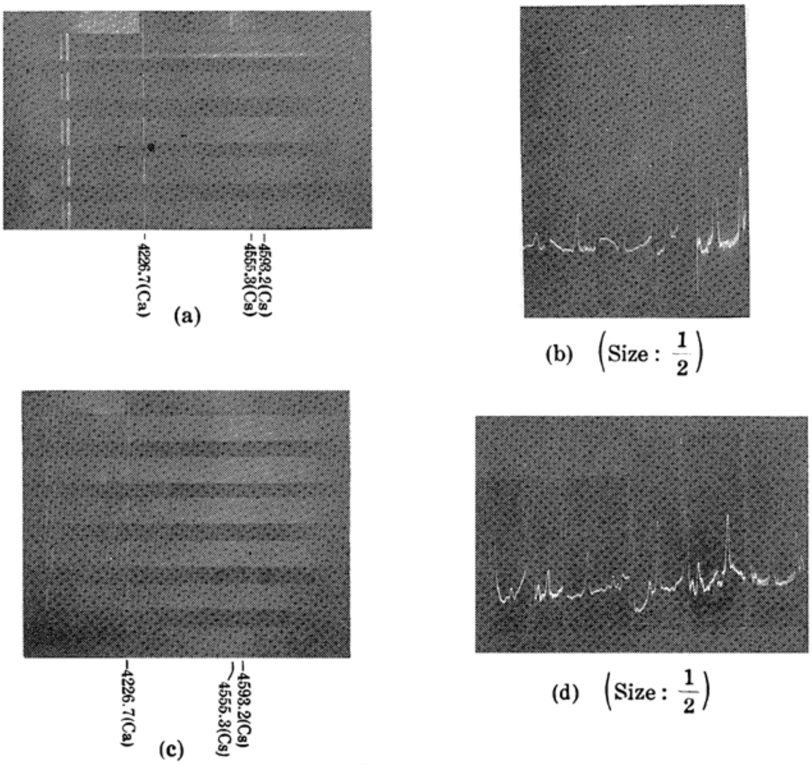
Another solid sample obtained from a plant was analysed by the density-percentage composition method and was found to contain 0.008% of caesium (or 0.011% as caesium chloride).

Another sample was similarly analysed and the content of CsCl was found to be 0.0143% as against the calculated value of 0.0150% (see Fig. 4, c and d), while by the graphical method from the density-percentage composition relation it was found to be 0.0155% as shown in Table 4.

Table 4.

No.	CsCl value	Method of comparison	%	Density-% relation	$\varDelta$ (%)
1	0.0005	0.00052	4.0	0.0006	20.0
2	0.0030	0.0029	−3.3	—	—
3	0.0150	0.0143	−4.6	0.0155	4.1
4	—	—	—	0.011	—

Thus it is seen that both methods of analysis may be adopted for determining the amount of caesium chloride contained in solid electrodes with the results which agree with each other and also with the calculated value fairly well.



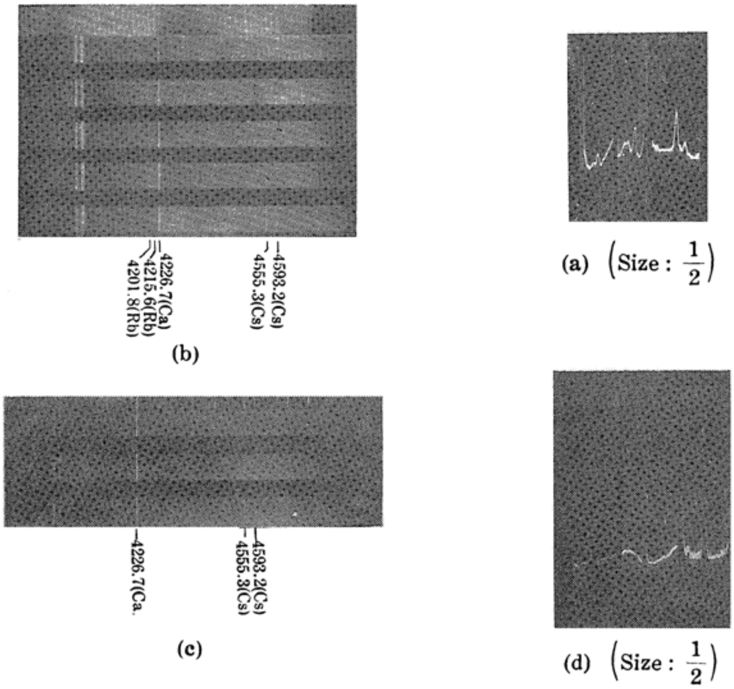
(a)

(b) $\left(\text{Size}: \frac{1}{2}\right)$

(c)

(d) $\left(\text{Size}: \frac{1}{2}\right)$

Fig. 3.



(a) $\left(\text{Size}: \frac{1}{2}\right)$

(b)

(c)

(d) $\left(\text{Size}: \frac{1}{2}\right)$

Fig. 4.

Summary.

(1) Solid sample electrodes were prepared from a caesium chloride solution, carbon and "sirupus simplex", and the amount of caesium chloride was spectrographically determined with a sensitivity of $2 \times 10^{-4}\%$.

(2) The analysis was conducted on sample electrodes containing 0.0005–0.015% of CsCl.

(3) Both the "method of comparison" and the graphical method were found to be applicable for the determination of caesium chloride with a fair degree of exactness, error being always caused within the permissible limit.

In conclusion, the present writer wishes to express his heartfelt and sincere thanks to Prof. M. Kimura, Phys. Inst., Imp. Univ. of Kyoto, for his supplying the writer with so many facilities during the years of experiment. Again, the writer wishes to express his high appreciation of the grant from the Imperial Academy towards this research.