Quantitative Spectral Analysis. X.
Determination of Lithium by Emission-Spectra.

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I. **Introduction.** Although the process is very tedious, the ordinary chemical method employed for the estimation of lithium contained in a sample solid is less reliable in outcome, principally owing to the difficulty of separating it completely from other alkalies. The present writer tried to establish the direct method for the quantitative analysis of lithium by means of emission-spectra and then to apply the method to some sample clay, produced in the prefecture of Aichi, commonly employed as raw materials of the ceramic industry in our country.

II. **Sample Electrodes.** Sample solid electrodes containing varying amounts of lithium chloride were prepared from carbon, lithium chloride and "sirupus simplex" by the method described in the preceding paper.(1) The lithium chloride taken for the experiment was obtained from Schering-Kahlbaum.

Sample electrodes containing clay were prepared by using the following mixture: 5 g. of clay (dried and powdered), 5 g. of carbon ("Nolit"), 10 c.c. of "sirupus simplex", and varying amounts of lithium chloride.

III. **Apparatus and Method of Experiment.** To excite arcs between a pair of electrodes, 220 volts alternating current was used. Self-inductance of a magnitude of 6000 cm. was inserted in the circuit. The light emanating from an arc between the sample electrodes was focussed on the slit of a glass-spectrograph of Nippon Kagakukikai Seisakusho make. The dispersion of the spectrograph was 96 Å per mm. at $\lambda = 6707.9$ Å.

The lithium lines at $\lambda = 6707.9$, 6103.6, 4971.9, and 4602.2 Å were detected, the first being the most sensitive.

The method of analysis was quite similar to that employed in the analysis of caesium reported in the preceding paper.(1)

IV. **The Sensitivity of the Sepectrographic Analysis.** The sensitivity of the spectrographic analysis of lithium chloride contained in a solid sample was thoroughly studied in the same way as was described in the previous paper.(2) The relation between the amount of lithium chloride contained in the solid sample and the intensity of the lithium line at $\lambda = 6707.9$ Å is shown in Table 1 and Fig. 1, d representing the galvanometer deflection measuring the intensity of the line.

Table 1.

LiCl (%) $\times 10^{-4}$	d (mm.)		Ratio (2)/(1)
	6707.9 Å (1)	6103.6 Å (2)	
0	1.5	1.8	1.2 (?)
1	4.3	1.8	0.42^{-}
2	5.7	2.0	0.35
3	10.0	2.6	0.26
4	11.9	4.0	0.34^{-}
8	19.0	6.5	0.34
			mean : 0.34

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(1) This Bulletin, **13** (1938), 260.

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

The dotted-line in Fig. 1 denotes the density of the back ground of the plate and the broken line denotes the density of the lithium line emitted from the very minute trace of lithium contained in the electrode material originally.

The spectrogram shown in Fig. 2, a, and the corresponding microphotometer record Fig. 3, a–f, show that the sample contains very minute trace of lithium, i.e. $2 \times 10^{-5}\%$. (See also Fig. 1.)

The sensitivity was thus found graphically to be 0.00003% under the conditions of the experiment. The sensitivity with respect to the line at $\lambda = 6103.6$ Å was found analogously to be 0.0001%. See also the spectrogram and the corresponding microphotometer records shown in Fig. 2, a, and Fig. 3.

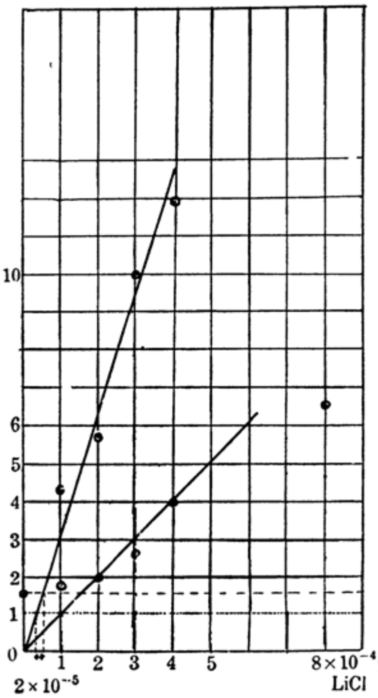


Fig. 1.

The ratio $d(2)/d(1)$ is calculated to be 0.34^{+} at a range of lithium chloride content varying from $1 \times 10^{-4}\%$ to $8 \times 10^{-4}\%$ as is shown in the 4th column of Table 1.

If the amount of lithium chloride to be determined is supposed to be exceedingly small, say $1 \times 10^{-4}\%$ to $3 \times 10^{-3}\%$, then the most sensitive line at $\lambda = 6707.9$ Å is to be selected. If lithium is contained in a larger amount the line at $\lambda = 6103.6$ Å should be selected. When the amount of lithium to be determined is much larger, say 0.005–0.05%, weaker excitation should be used, i.e. uncondensed high-tension spark or flame excitation. Fig. 2, b, is an example of uncondensed spark excitation adopted in the determination of lithium content as much as 0.05%. Spectrograms in Fig. 6 and Fig. 7 show how the line at $\lambda = 6707.9$ Å should not be used, because the intensity of the line does not vary as the percentage composition varies.

V. **Examples of Analysis.** The results of analysis showing how the method of comparison may be employed for the analysis, turned as follows:

Let S denote the percentage of LiCl in the sample taken, Δ the percentage deviation from the calculated value.

Ex. 1. $S = 0.0010\%$.

LiCl (%)	d (mm.) $\lambda = 6707.9$ Å
0.0005	17.4
	2.6
S	20.0
	5.1
0.0020	25.1

By proportion we get, $15 \times \frac{2.6}{7.7} = 5.1$.

$\therefore \quad S = 0.0005 + 0.00051 = 0.00101$.

$$\Delta = 100 \times \frac{1}{100} = 1.0\%.$$

Ex. 2. $S = 0.0025\%$.

LiCl (%)	d (mm.) $\lambda = 6707.9$ Å
0.0010	20.2
	10.1
S	30.3
	5.2
0.0035	35.5

By proportion we get, $25 \times \frac{10.1}{15.3} = 16.5$.

$\therefore \quad S = 0.0010 + 0.00165 = 0.00265$.

Another sample was analysed by exciting the sample electrodes with uncondensed sparks and the content of lithium chloride was found to be 0.0475% as against the calculated value of 0.0450%, the error being $100 \times \frac{25}{450} = 5.5\%$. (See Fig. 2, b.)

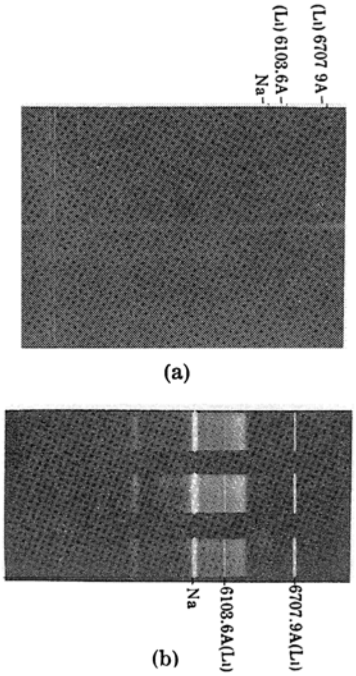
The results of analysis by the graphical method of applying the density-percentage composition relation is shown in Tables 2–4 and the spectrograms and their corresponding microphotometer records being given in Fig. 6 and Fig. 7.

The density-concentration method is favourably applicable in a range only, where the relation $d \propto c$ holds. With respect to the line at $\lambda = 6707.9$ Å, these spectrograms are over-exposed or over-developed and they show that the densities do not vary proportionally as the content of lithium varies, while the line at $\lambda = 6103.6$ Å is normally exposed or normally developed. For this reason the line at $\lambda = 6103.6$ Å has been selected in the determination of lithium in the following cases. The reason why the ratio of (2)/(1) is not constant is also self-evident.

Table 2.

LiCl (%) $\times 10^{-2}$	d (mm.)		Ratio (2)/(1)
	6707.9 Å (1)	6103.6 A (2)	
x	20.9	1.7	0.08
1	23.6	3.3	0.14^{-}
2	24.6	5.9	0.24^{-}
3	34.0	12.0	0.35

$x = 0.001\%$ or $1 \times 10^{-3}\%$.



(a)

(b)

Fig. 2.

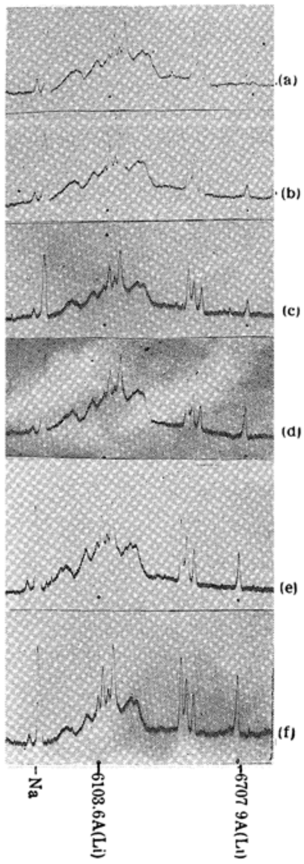


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Fig. 3.

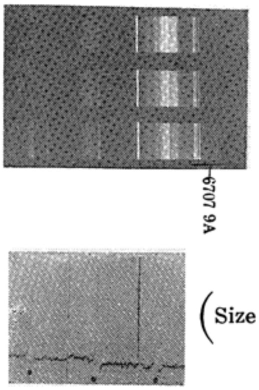

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Fig. 4.

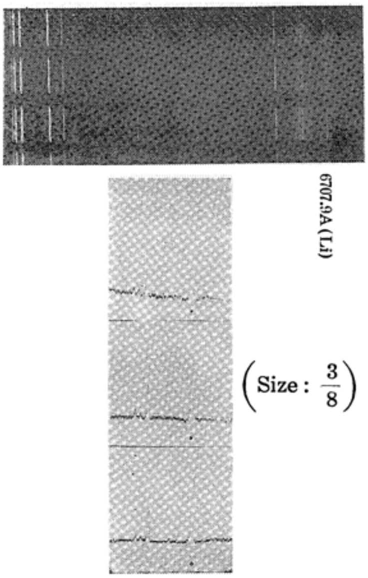

Fig. 5.

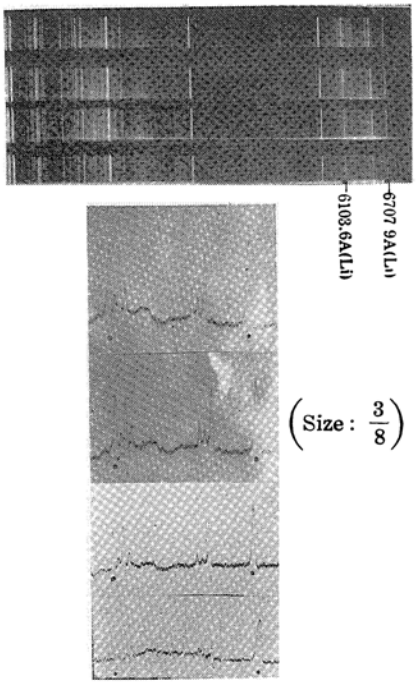

Fig. 6.

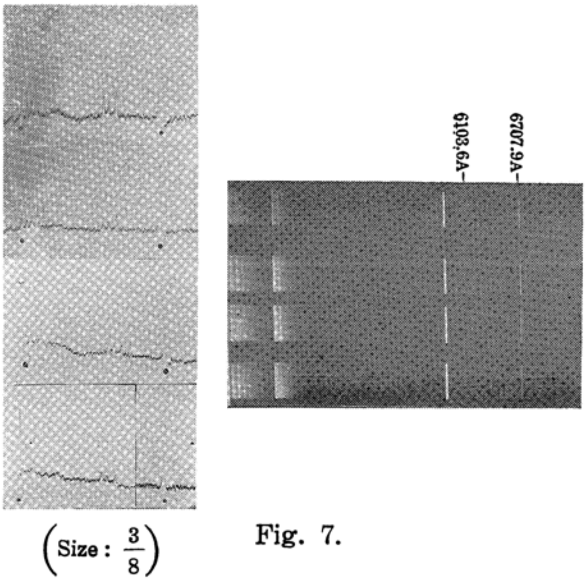

Fig. 7.

Table 3.

LiCl (%) $\times 10^{-4}$	d (mm.)		Ratio (2)/(1)
	6707.9 Å (1)	6103.6 Å (2)	
x	32.4	4.9	0.15
1	34.5	8.4	0.24
2	44.5	17.8	0.40
3	46.4	18.8	0.45^{-}

$x = 0.005\%$ or $5\times10^{-3}\%$.

Table. 4.

LiCl (%) $\times 10^{-3}$	d (mm.)		Ratio (2)/(1)
	6707.9 Å (1)	6103.6 Å (2)	
x	14.3	6.2	0.43
2	19.5	12.2	0.63^{-}
4	23.6	19.0	0.81^{-}
8	27.9	21.9	0.78

$x = 0.012\%$ or $12\times10^{-3}\%$.

The results of analysis is shown in Table 5.

Table 5.

No.	Comp. method found (%)	Calc. value (%)	Δ (%)	No.	Density-conc. relation $\times10^{-3}$ (%)
1	0.00101	0.0010	1.0	5	1
2	0.00265	0.0025	6.0	6	5
3	0.0052	0.0050	4.0		
4	0.0475	0.0450	5.5	7	12

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

In case, the lithium lines are observed in the spectrum of the carbon electrodes, the determination of lithium may be carried out by the method analogous to that previously described.⁽³⁾

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(3) A. Iwamura, *Mem. Coll. Sci., Kyoto Imp. Univ.*, A, **14** (1931), 332.

Summary.

(1) Solid sample electrodes were prepared from carbon, "sirupus simplex" and varying amounts of lithium chloride, and the amount of lithium chloride was spectrographically determined with a sensitivity of $3 \times 10^{-5}\%$ with respect to the line at $\lambda = 6707.9$ Å, and with that of $1 \times 10^{-4}\%$ with respect to the line at $\lambda = 6103.6$ Å.

(2) The method of comparison was found to be applicable for the determination of lithium chloride throughout the range of 0.001–0.050%.

(3) Several samples containing lithium were analysed by the graphical method and were found to contain $1—12 \times 10^{-3}\%$ of lithium chloride.

(4) Several samples of clay produced in Seto and Inuyama were found to contain $3 \times 10^{-5}\%$ of lithium by the graphical method.

In conclusion, the writer wishes to express his high appreciation of the grant from the Imperial Academy towards this research.