

## Lead Content of the Calcareous Sinters.

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The calcium carbonate precipitated from hot-springs carries down a great variety of impurities characteristic to each hot-spring. In the calcareous deposits from the springs of Vichy, for example, J. Bouquet<sup>(1)</sup> found the presence of arsenic. W. P. Headden<sup>(2)</sup> reported that tufa from the Doughty springs, in Colorado, probably contained traces of radium. The radium content of a number of sinter deposits from radioactive mineral springs in Japan was recently estimated by T. Nakai,<sup>(3)</sup> and the thorium content of sinter from Masutomi by K. Shimokata.<sup>(4)</sup> Hokutolite, found from the hot springs of Hokuto in Formosa for the first time, consists of barium and lead sulphate and is strongly radioactive. In the calcareous sinters, however, lead is rarely detected. E. Minami and K. Hirabayashi<sup>(5)</sup> estimated the zinc content of sinters from a number of hot-springs in Japan by the polarographic method. These sinters contained a minute quantities of zinc (0.0000–0.0007%), but no samples contained a detectable amount of lead. The present author has studied the sinters from the hot-springs of Yunomata in the Japanese Northern Alps, which were collected and sent to us through the courtesy of Dr. S. Oana. The author was able to estimate the lead content by the polarographic method, though the presence of lead was not detected spectroscopically. (\*)

The sinters were faintly rose coloured and was supposed to contain a considerable amount of manganese. One sample was gray coloured and Dr. Oana said that it contained iron sulphide. They dissolve quite readily in hydrochloric acid and have no visible insoluble residue.

5 g. of sample were dissolved in hydrochloric acid (distilled) and the solution was evaporated to dryness. The residue was carefully dissolved in water and the solution was made up to 10 c.c. A part of the solution was put in a small electrolysis vessel and then polarographically examined, using a 2-volts accumulator. The solution brought to the electrolysis vessel was yellow coloured and the current-voltage curve showed a large wave at the beginning (Fig. 1). Between the 5th and the 6th lines a fine "lead-wave" is seen. The height of this wave is about 5 mm. (sensitivity of the galvanometer=1/20) (Fig. 2). The height of

(1) J. Bouquet, *Ann. chim. phys.*, (3) **42**(1854), 332.

(2) W. P. Headden, *Proc. Colorado Sci. Soc.*, **8**(1905), 1.

(3) T. Nakai, this Bulletin, **15**(1940), 333.

(4) K. Shimokata, *J. Chem. Soc. Japan*, **63**(1942), 1109.

(5) Not yet published.

(\*) According to Prof. K. Kimura, less than 1  $\gamma$  lead in 10 mg. sample can not be detected by usual spectroscopic method. As the lead content of this sinter is less than 0.01%, 10 mg. of sample contains less than 1  $\gamma$  of lead. Therefore the presence of lead was not detected spectroscopically.

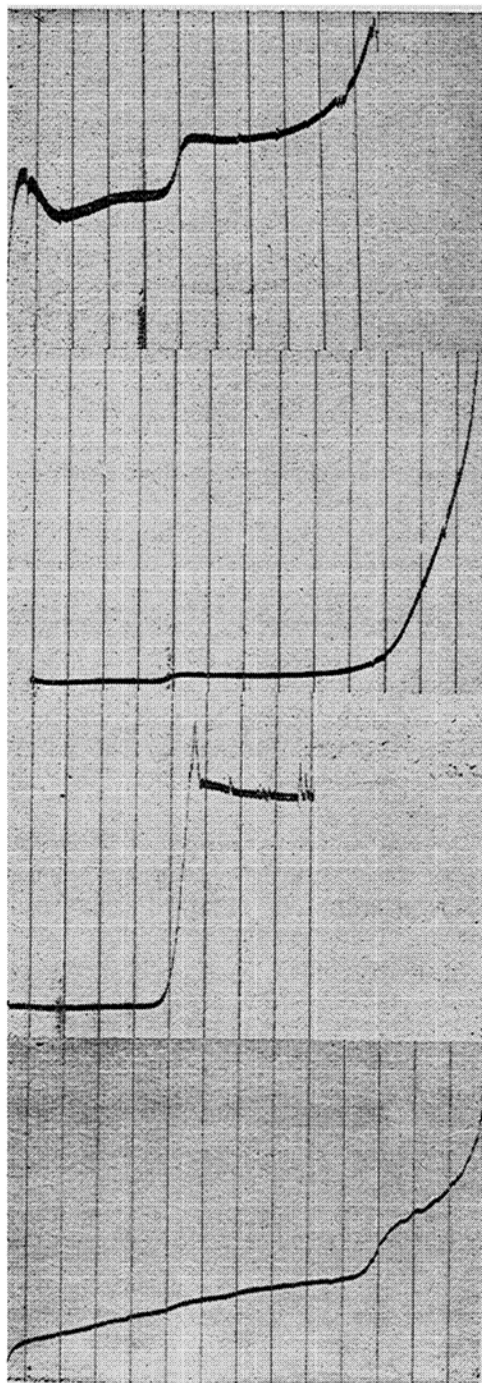


Fig. 1. Calcareous sinter from the hot springs of Yunomata.

Sensitivity of the galvanometer  $1/5$ .  
2 volts accumulator.

Fig. 2. Calcareous sinter from the hot springs of Yunomata.

Sensitivity of the galvanometer  $1/20$ .  
2 volts accumulator.

Fig. 3. Calcareous sinter from the hot springs of Yunomata.

A little lead nitrate solution was added.

Sensitivity of the galvanometer  $1/20$ .  
2 volts accumulator.

Fig. 4. Pure calcium carbonate for analytical use.

Sensitivity of the galvanometer  $1/5$ .  
2 volts accumulator.

the wave increased when a little lead nitrate solution was added (Fig. 3). The height of wave became 116 mm when 3.1 mg. of Pb was added. The lead content of this sinter is, therefore, considered to be 140  $\gamma$  per 5 g., namely 0.0028%.

Pure calcium carbonate for analytical use was equally treated and polarographically examined. The presence of Zinc was detected and the amount was estimated to be about 0.0016%. Lead was, however, not detected in this sample. This experiment shows that the reagents which were used in this experiments did not contain lead.

As the radium content of the water and the calcareous sinter is not yet known, we can not discuss the relation between the content of lead and the radioactivity of the hot-spring in this paper. The radium content of this calcareous sinter will be reported shortly.

### Summary.

The lead content of the calcareous sinter from the hot-springs of Yunomata in Northern Alps, Nagano Prefecture was estimated by the polarographic method.

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