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A SPECTROGRAPHIC METHOD FOR DETERMINING TRACE AMOUNTS OF LEAD IN ZIRCON AND OTHER MINERALS

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A SPECTROGRAPHIC METHOD FOR DETERMINING TRACE AMOUNTS OF LEAD IN ZIRCON AND OTHER MINERALS

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ABSTRACT

The spectrographic determination of lead in zircon and in some other minerals has been made by the U. S. Geological Survey to provide data in a study of the age of the rocks that contained these particular minerals. Approximately 150 determinations have been made, and one reproducibility test (consisting of 25 observations) has been completed. The material used for the reproducibility test was a silica-base standard containing 30 ppm lead. The average of the results was 30.4 ppm lead. On the whole, standard spectrographic procedures were applied, including the split-filter method for calibrating the photographic emulsions.

The method is applicable to samples containing from 0.5 to 1,000 ppm lead with an estimated accuracy of from 6 to 10 percent. No chemical separations or concentrations are required. The other minerals tested by the method are apatite, sphene, microlite, allanite, and perthite.

INTRODUCTION

The present work of E. S. Larsen, Jr.,[1] in using the accessory minerals of granites for geologic age determinations is based on

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[1] Larsen, E. S. Jr., Keevil, N. B., Harrison, H. C., A method of determining the age of igneous rocks using the accessory minerals (in preparation); Abstract in Geol. Soc. America Bull., vol. 61, p. 1480, 1950.

ascertaining total radioactivity and total lead. This necessitated a precise and sensitive spectrographic method for the determination of lead in zircon and in other minerals and resulted in the development of a method that is sensitive to as little as 0.5 ppm lead. To a great extent standard spectrographic procedures have been applied.

Various fluxes, sample weights, types of standards, electrodes, power sources, spectrographic emulsion types, and spectrographs were used in developing the method. The problem revolved around two difficulties, one of which was lead impurities in the chemicals and electrodes (especially in copper electrodes), and the other, the insensitivity of lead in very low concentrations. These problems were solved by systematic elimination and trial-and-error procedures. It was found that, using National special graphite spectroscopic electrodes, an alkaline vapor (sodium carbonate) with type II-O Eastman spectrographic emulsion would record the 2833.1 A line at a concentration of 0.5 ppm.

The authors wish to express appreciation to their associates of the U. S. Geological Survey, especially to E. S. Larsen, Jr., for providing many of the samples and offering valuable suggestions. This work was done on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission.

OUTLINE OF METHOD

A method is provided for determining the lead content of zircon samples in the range of 0.5 to 1,000 ppm lead. It is thought that higher percentages of lead can be determined by applying the same procedure but with changes in transmission and line selection.

The method involves weighing a 12.5-mg sample, mixing with three parts by weight of sodium carbonate, subjecting the sample and suitable standards to an interrupted d-c arc excitation in National special graphite spectroscopic electrodes, processing the plate, reading with the densitometer, calibrating the emulsion and making final calculations.

Procedure

Apparatus

Excitation source - Applied Research Laboratories, Multisource interrupted d-c arc.

Spectrograph - Jarrell-Ash 21-foot, Wadsworth-mounted grating, 5 A per mm.

Intensity control - Applied Research Laboratories neutral filters and split filter (stainless steel on quartz).

Developing equipment - Applied Research Laboratories rock developing tank, plate washer, and drier.

Electrode cutters - A. Lower electrodes, designed to cut ¼-inch electrodes (outside diameter 0.22 inch, inside diameter 0.19 inch, depth of crater 0.24 inch, depth of shoulder 0.24 inch). National special graphite spectroscopic electrodes.

b. Upper electrodes, hemispherical 0.06-inch radius. National special graphite spectroscopic electrodes.

Densitometer - Jarrell-Ash, nonrecording, or Leeds and Northrup, recording.

Preparation of standards

Standards were prepared by adding solutions of pure lead nitrate to a lead-free base material (silicic acid). The mixtures were evaporated to dryness in platinum crucibles and ground in a boron carbide mortar to pass 100-mesh stainless-steel screen. Mixing was accomplished by passing the material through an 80-mesh stainless-steel screen approximately 15 times. The standards were prepared to contain the following concentrations of lead in ppm: 1, 5, 15, 30, 50, 75, 100, 200, 500, 750, and 1,000. A blank of the base material was similarly processed to determine whether it was contaminated with lead.

A mixture of sodium carbonate and lead-free bismuth, as internal standard, was added to mineral samples which were then excited in an alkali vapor. This mixture was prepared by adding 0.1 percent bismuth 2/ (or 0.05 percent bismuth for determining low percentages of lead) to approximately 2 g lead-free sodium carbonate,3/ and this was processed in the same manner as the standards. The electrodes were loaded with a mixture consisting of 12.5 mg of the standard and 37.5 mg of the sodium carbonate and bismuth mixture.

The mineral samples were ground in a boron carbide mortar to pass 100-mesh stainless-steel screen. In arcing, the loaded electrode contained 12.5 mg of sample and 37.5 mg of the sodium carbonate and bismuth mixture.

2/ Prepared by dissolving "Specpure" bismuth metal in lead-free nitric acid.

3/ Sandell, E. B., Colorimetric determination of traces of metals, Interscience Publishers, p. 295, 1944.

Analysis of unknowns

The samples and suitable standards are placed in the electrode cups (positive) with the aid of a special glass funnel. The electrodes were arced for a period of 120 seconds, and the gap held constant at 6 mm by manual adjustments. The following Multisource conditions and photographic procedures were used:

Capacitance	60 microfarads
Inductance	400 microhenries
Resistance	15 ohms
Initiator	high
Phase	0
Strike	strike position
Amperes	12 (± 0.5)
Spectrograph	Jarrell-Ash
Emulsion	SA-1 (Eastman)
Photographic development	4 minutes at 18°C ± 0.5°, D-19
Slit	50 microns
Volts	300
Intensity control	variable
Electrodes	National special graphite spectrographic electrodes

After processing the plates, the transmission values of the following lines were read by applying the Jarrell-Ash nonrecording or Leeds and Northrup recording densitometers:

Bismuth	**Lead**
2938.3 A	2833.1 A
2898.0 A	2823.2 A
	2802.0 A
	2663.2 A
	2614.2 A

After numerous tests the lead line 2833.1 A and bismuth line 2898.0 A were selected for use because these lines approach homologous pair conditions.

Emulsion calibration

In calibrating the emulsion a two-step method was used. Similar methods, in which a split filter has been substituted for the rotating sector, have been described by other authors.[4,5] The split filter (stainless steel on quartz) is an improvement over the step sector because it minimizes or eliminates such well-known disadvantages as stroboscopic, intermittency, and target effects which are prevalent in the step-sector method.

Calculations

The working curves prepared from the standards served as a check on the standards but were not used in the calculations of final results. The standards indicated reliability by the straightness of the line drawn through the points that were obtained by plotting the relative intensity against the logarithm of the lead concentration.

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[4] Harvey, C. E., Spectrochemical procedures, Applied Research Laboratories, pp. 76-78, 1950.

[5] Churchill, J. R., Techniques of quantitative spectrographic analysis: Ind. and Eng. Chemistry, Anal. Ed. 16, pp. 664-665, 1944.

By preliminary survey the parts per million of lead were estimated. Standards to bracket the lead content of the samples and the samples themselves were exposed on the same plate. The parts per million lead were then calculated, employing the x and y coordinates of the relative intensities versus parts per million lead. This method of calculation has the advantage of using a short section of a curve with samples closely bracketed by standards on the same plate.

No background corrections were necessary, as the background at the lead and bismuth lines were insignificant.

Reproducibility of results

Few data have been collected on the reproducibility of the results obtained by the method. The data on one test, consisting of 25 observations of the 30 ppm lead standard in silica base, are shown in table 1. The maximum variation is 5 ppm lead in 1 observation, and there was no variation in 9 observations. The average of the 25 observations is 30.4 ppm lead.

Reproducibility of results on some of the lead determinations made at different times is shown in table 2.

Table 1.--Reproducibility data on 30 ppm lead in silica base

Observation	Lead ppm	Difference
1	31	1
2	30	0
3	33	3
4	30	0
5	34	4
6	30	0
7	29	1
8	30	0
9	28	2
10	28	2
11	28	2
12	29	1
13	30	0
14	30	0
15	32	2
16	28	2
17	31	1
18	30	0
19	35	5
20	32	2
21	30	0
22	29	1
23	30	0
24	31	1
25	32	2

Table 2.--Reproducibility of results of lead determinations on some of the zircon samples

Sample no.	Parts per million lead 1st run	 2d run	 3d run	 4th run
Z-1	86	89		
Z-3	40	38		
Z-5	50	49		
Z-6	33	27	28	33
Z-7	35			
Z-8	18			
Z-9	25	24	23	
Z-11	130	121	127	
Z-40	3			
Z-42	4			

A zircon sample from Tory Hill, Haliburton area, Ontario, was checked for lead by the isotope dilution method of Brown, Patterson, and Inghram, University of Chicago, and found to contain 451 ppm lead. By applying the method described in this paper to duplicate samples of the same material 462 and 437 ppm lead were determined. Also a Canadian perthite sample ran 6.7 ppm lead by the isotope dilution method and 5 ppm lead spectrographically.

It is hoped that microchemical and mass spectrographic techniques will be developed to provide further checks on this method. The precision of the method is estimated to be 6 to 10 percent.

DISCUSSION

During the course of the analysis it was thought that certain lead results on zircon samples might be high. A microscopic examination of the samples showed foreign particles. Spectroscopic inspection of these particles indicated a high percentage of lead. As the lead in the zircon crystals was of primary interest, it became necessary to treat the samples with aqua regia to remove the foreign particles of high lead content which occurred naturally in the samples. This treatment with aqua regia is still in the experimental stage but will probably become a part of the standard procedures because encouraging results have been obtained.

Figures 1 and 2 are typical examples of working curves obtained by the described method. Some acceptable curves were also obtained by plotting transmission against lead (in ppm); this leaves some doubt as to the necessity of an internal standard. Additional tests will be conducted before any conclusions are drawn.

As the chances of contamination are great, the method was designed to reduce the handling of samples to a minimum. It was found that grinding a sample in the agate mortar added a few parts per million lead to the sample, but no lead contamination was detected after grinding the same in a boron carbide mortar. No lead contamination was detected from the stainless-steel screens, but screening through nylon cloth added a few parts per million lead.

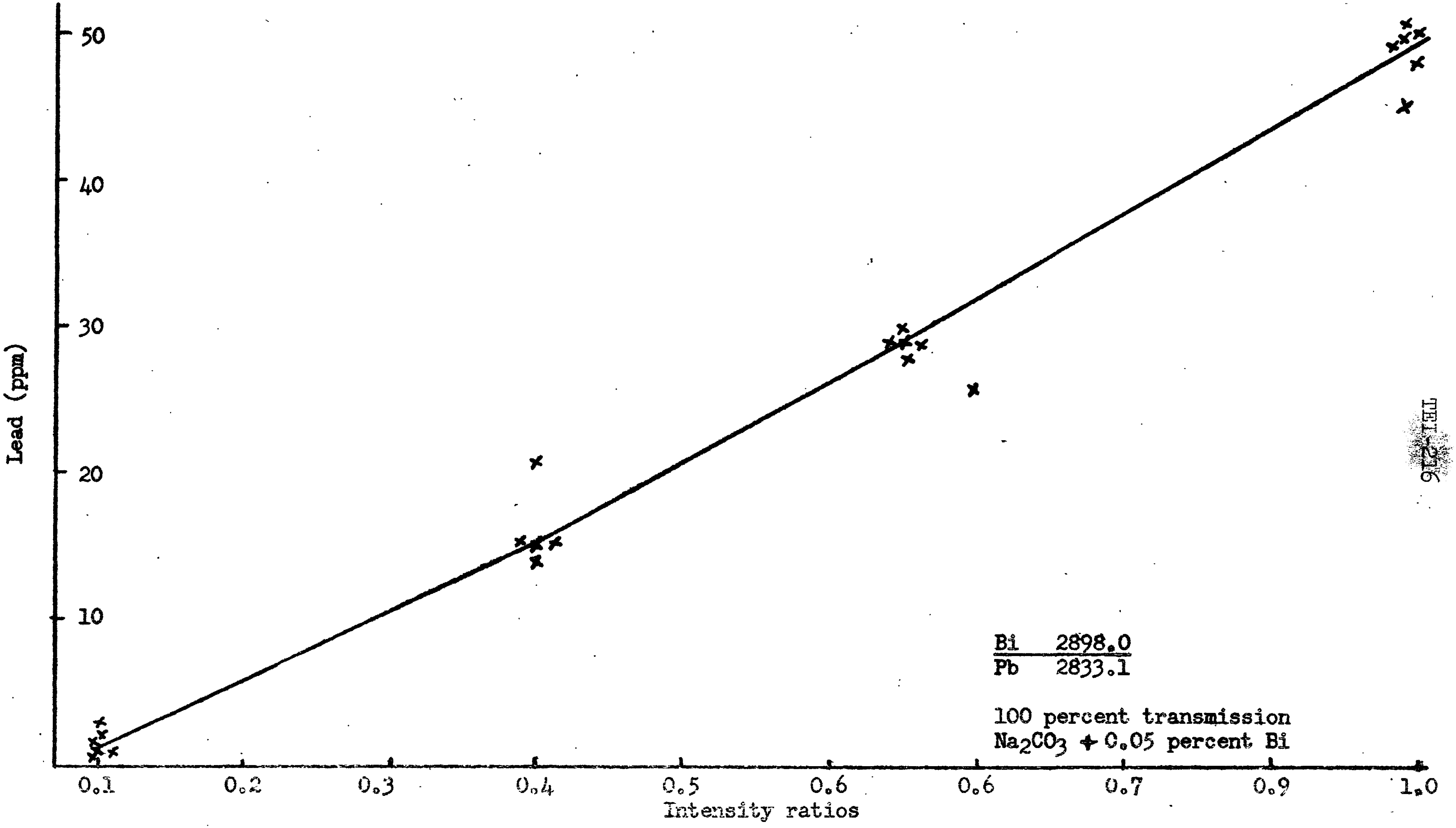

Figure 1.--Working curve for lead in zircon, applied in the ranges 1-50 ppm lead

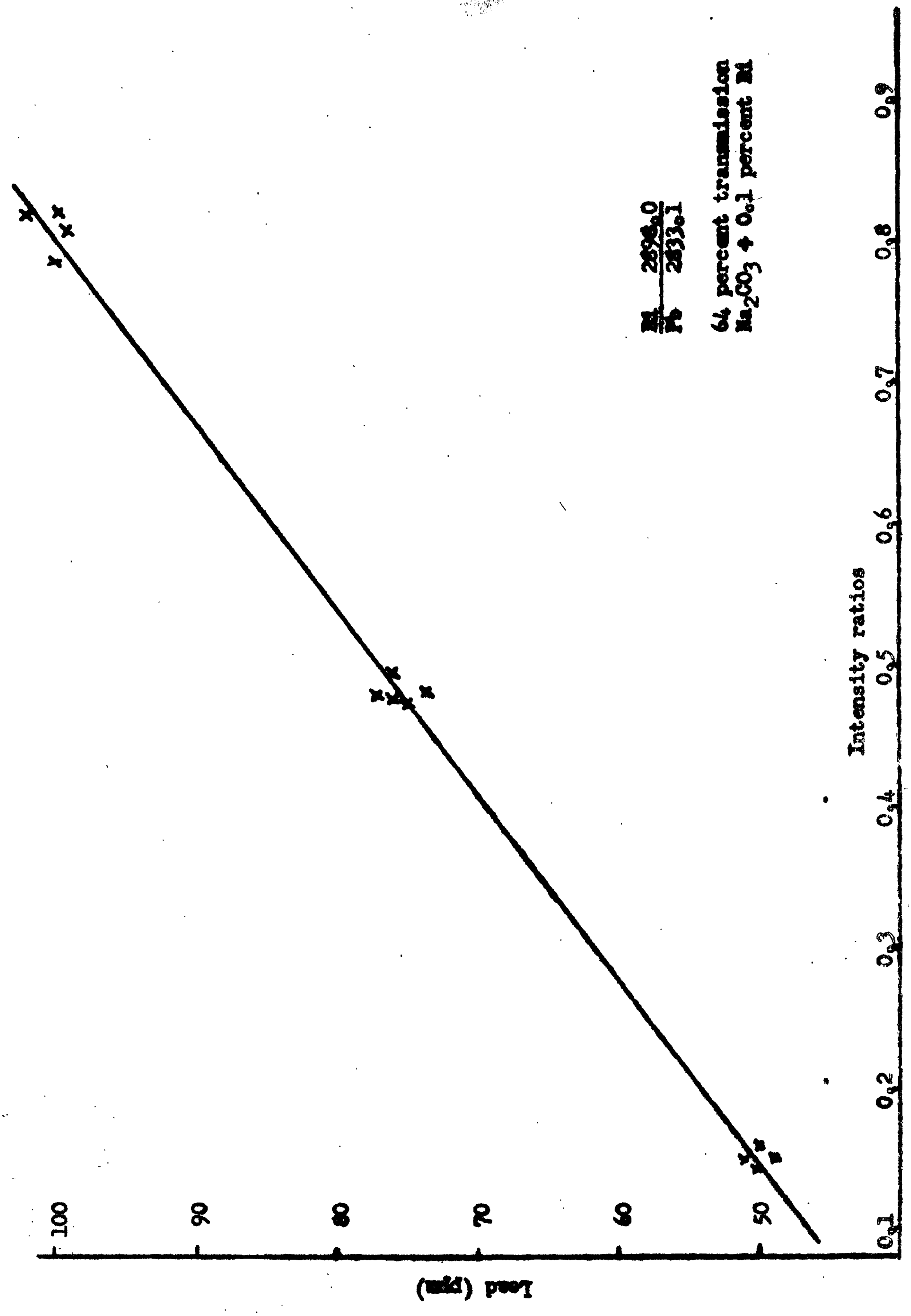

Figure 2.--Working curve for lead in zircon, applied in the range 50-100 ppm lead

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