A SPECTROGRAPHIC METHOD FOR DETERMINING THE HAFNIUM-ZIRCONIUM RATIO IN ZIRCON

By C. L. Waring and H. W. Worthing

Trace Elements Investigations Report 502

UNITED STATES DEPARTMENT OF THE INTERIOR

GEOLOGICAL SURVEY

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IN REPLY REFER TO:

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DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY
WASHINGTON 25, D. C.

AEC-642/5

February 28, 1955

Mr. Robert D. Nininger, Acting Assistant Director
Division of Raw Materials
U. S. Atomic Energy Commission
Washington 25, D. C.

Dear Bob:

Transmitted herewith are three copies of TEI-502, "A spectrographic method for determining the hafnium-zirconium ratio in zircon," by C. L. Waring and H. W. Worthing, February 1955.

We are asking Mr. Hosted to approve our plan to submit this report for publication in Analytical Chemistry.

Sincerely yours,

for John H. Eric
W. H. Bradley
Chief Geologist

JAN 23 2001

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Series A.

UNITED STATES DEPARTMENT OF THE INTERIOR

GEOLOGICAL SURVEY

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This preliminary report is distributed without editorial and technical review for conformity with official standards and nomenclature. It is not for public inspection or quotation.

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*This report concerns work done on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission.

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A SPECTROGRAPHIC METHOD FOR DETERMINING THE HAFNIUM-ZIRCONIUM RATIO IN ZIRCON

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ABSTRACT

To develop a rapid spectrographic method for the determination of hafnium and the hafnium-zirconium ratio in the mineral zircon, the ratio was determined first by plotting the log of the intensity ratios against the log of the hafnium-zirconium ratio by weight of the standards, using zirconium as an internal standard. Straight-line curves were produced when the same line pairs (zirconium 2538.405A and hafnium 2641.406A) were used in a similar manner for the hafnium determinations. After the hafnium-zirconium ratios and the hafnium percentages were determined, the zirconium percentages were calculated. When chemical methods were used to check the spectrographic hafnium and zirconium totals, an apparent bias of +1.87 was observed. The results of a limited series of tests indicate a precision of within 10 percent.

INTRODUCTION

In connection with a study of the radioactivity and geochemistry of minerals, rocks, and ores, a rapid spectrographic method was developed for the determination of the hafnium percentage and the hafnium-zirconium ratio of the mineral zircon. The mineral samples were highly purified and had hafnium contents ranging from 0.1 percent to several percent, and the zirconium content was approximately 50 percent.

The published spectrographic methods for determining the percentage of hafnium and hafnium-zirconium ratio have been reviewed by Ahrens (1). Many of these methods are applicable to rocks containing small amounts of zirconium and hafnium, after chemically concentrating these elements. The solution technique of Feldman (3) was not suitable as a rapid method for determining hafnium and the hafnium-zirconium ratio because of the difficulty of and time involved in dissolving the samples and preparing special electrodes.

The method described here consists of arcing (d-c) to completion 1 mg. of the solid sample and the synthetic standards, mixed with two parts by weight of spectrographically pure graphite, processing the plate, obtaining the intensities of selected hafnium and zirconium lines by means of the densitometer, preparing percentage and emulsion calibration curves, and calculating the results.

The method as written is not applicable to rock samples containing small amounts of zirconium. The sensitivity of hafnium is approximately 0.01 percent and would not be detected in samples of low zirconium content. It would be necessary either to separate the zirconium-containing minerals from the rock in order to apply the method or to improve the method in such a way as to increase the detection limit of the hafnium. Additional development work would be necessary to adjust the method to include the hafnium and hafnium-zirconium ratio of most rock samples.

STANDARDS

The chemicals used in preparing the synthetic standards were Specpure grade, Johnson, Matthey and Company. The zirconium content of the hafnium oxide was certified as 1.5 percent. According to the company's directions for using the spectrographically standardized hafnium oxide for the determination of the zirconium content, a small portion of the sample was added to pure titanium dioxide. The zirconium was then determined quantitatively as a minor constituent in the titanium dioxide. The percentage of zirconium was confirmed by the Geological Survey laboratory by using as a standard the oxide of pure zirconium metal (40 ppm hafnium, 800 ppm iron, 40 ppm nitrogen, remainder zirconium) supplied by the U. S. Bureau of Mines, Albany, Oregon.

A method of addition and extrapolation similar to that of Pierce and Nachtrieb (8) was applied to the zirconium oxide to determine the hafnium content. Numerous tests were run and the average taken to establish the percentage of hafnium in the zirconium oxide as 0.1 percent. This result compared favorably with the one obtained by the semiquantitative method (9) which is based on standard plates prepared with Specpure chemicals and which has been used in the Geological Survey laboratory for the past four years.

The silicon dioxide was prepared from silica plate, heated to 600° C, cooled quickly to fracture, ground to 100+ mesh, leached in aqua regia, and washed with distilled water.

Standards were prepared by adding known amounts of minor and trace elements as standard solutions to a mixture of 67 percent zirconium dioxide and 30 percent silicon dioxide. The minor and trace elements of several highly purified zircon samples were known from previous work (7). The moistened mixtures were dried in platinum dishes on a hotplate at approximately 100° C, ignited at 500° C, for four hours, and ground in a boron carbide mortar to pass 100-mesh stainless-steel screen. For more thorough mixing, the standards were passed repeatedly through 80-mesh stainless-steel screen. Six standards were prepared with hafnium contents of 0.2, 0.5, 1.0, 1.5, 2.0, and 2.5 percent, after corrections for the hafnium originally present in the zirconium oxide.

EXPERIMENTAL DATA

The usual procedure here is to consume at least 10 mg of sample in the arc for quantitative work. To consume completely this amount of the zircon mineral required a long period of burning because of the refractory nature of the zirconium. The long burning time of the 10 mg sample resulted in excessive background. It was later established that results obtained by incomplete burns were low as compared to the zirconium-hafnium totals given by chemical analysis. Several buffers were tried unsuccessfully. The above difficulties were solved by additional tests which showed that 1 mg of the sample mixed with two parts by weight of spectrographically pure graphite were completely consumed in the d-c arc in 180 seconds using a current of 12 amperes. We found, as Feldman (3) did, that the log of the intensity ratios plotted against the log of the hafnium-zirconium ratios by weight of the standards produced straight line curves that were considered satisfactory for determining the concentration ratios. Zirconium 2583.405 A as the internal standard and hafnium 2641.406 A were selected from several line pairs under study. Straight-line curves were produced when the same spectral lines were used to plot the log of the intensity ratios against the log

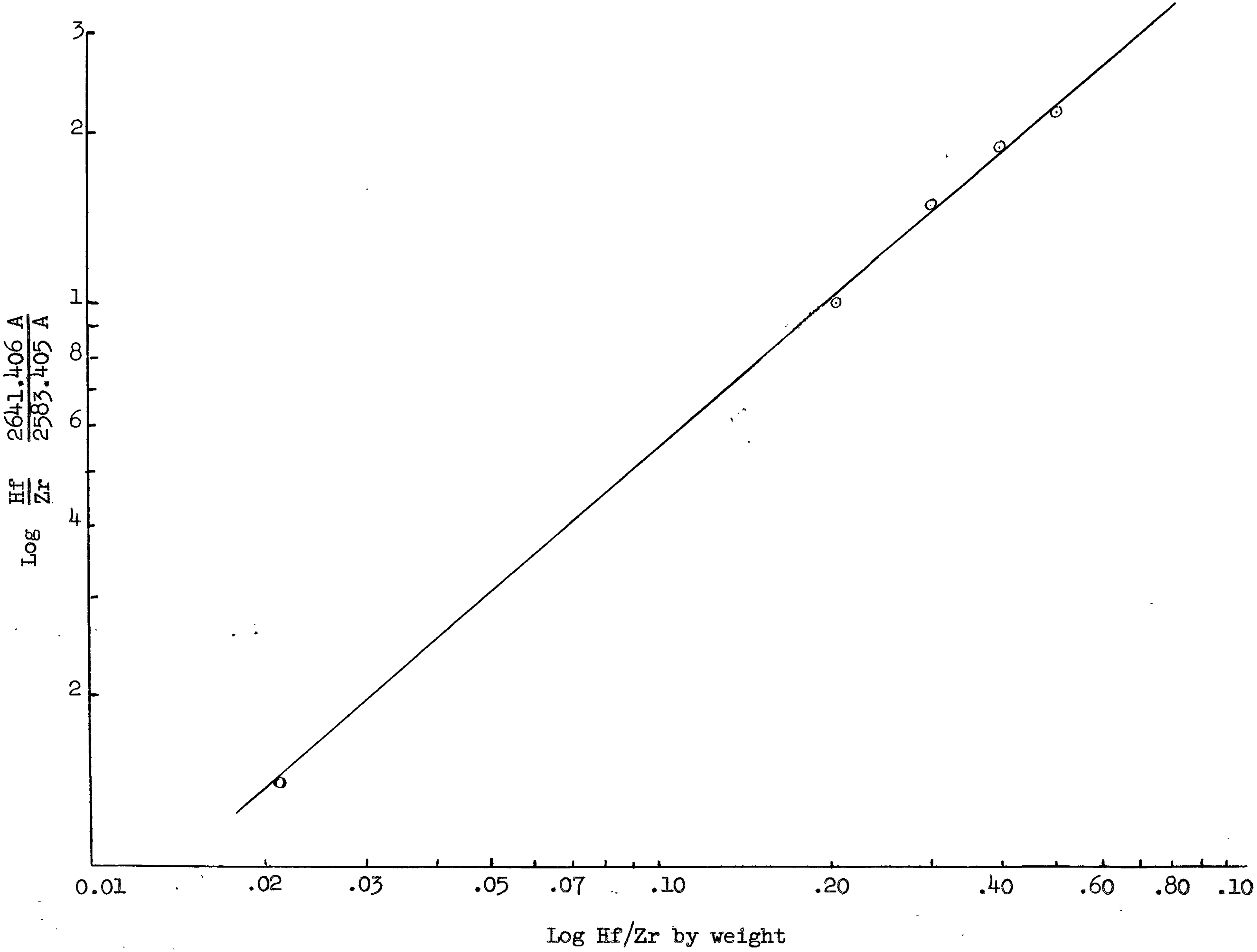

Figure 1.--Working curve of hafnium/zirconium ratio in zircon.

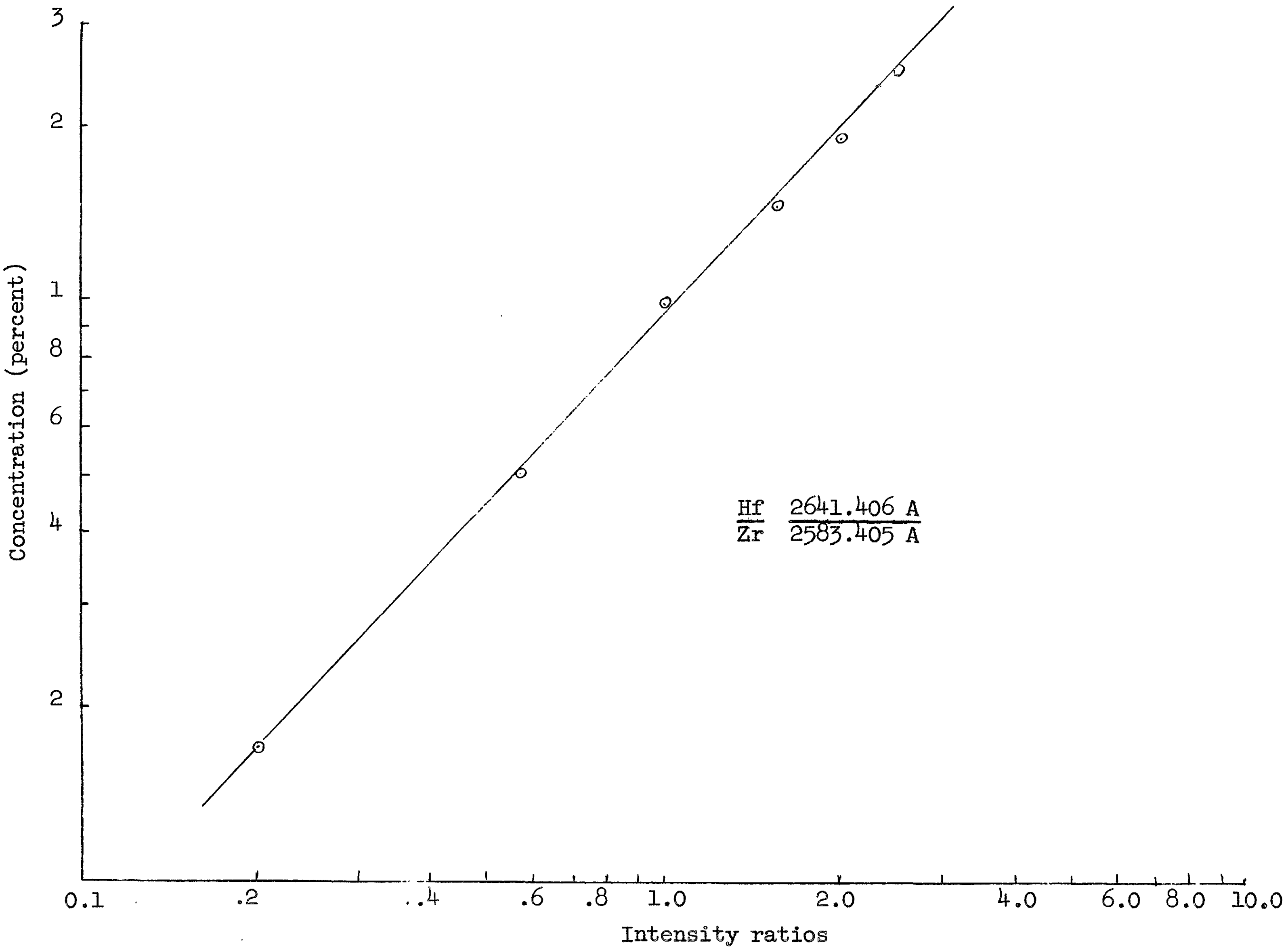

Figure 2.--Hafnium working curve.

percentage concentration of hafnium for the hafnium determinations. Figures 1 and 2 show typical examples of these curves.

The emulsion calibration curves were prepared by the two-step method of Churchill (2) and Harvey (4).

The following experimental conditions were used:

Excitation source, Multisource d-c arc.

Resistance, 15 ohms.

Initiator, high.

Phase, 0

Strike, strike position.

Amperes, 12

Spectrograph, 21-foot Wadsworth-mounted grating.

Slit, 25

Optics, arc image focused on grating.

Emulsion, SA-1 (Eastman).

Development, 5 minutes at 18° C, ± 1/2° C, D-19.

Arc gap, 4 to 6 mm

Transmission, 100 percent.

Arcing time, 3 minutes.

Electrode, lower, carbon, National regular spectroscopic carbons grade AGKS, 1/4 in., cut to outside diameter 0.22 in., depth of shoulder 0.12 in., inside diameter 0.19 in., depth of crater 0.12 in.

Electrode, upper, carbon, National regular spectroscopic carbons grade AGKS, 1/4 in., hemispherical, 0.06-in. radius.

EVALUATION OF RESULTS

Six samples were chemically analyzed by two methods for their contents of zirconium and hafnium. The first chemical method (5), precipitation by n-propylarsonic acid, gave precipitates with a high content of impurities, as shown by spectrographic analysis Chemical precipitates, produced by the mandelic acid precipitation method (6), were tested spectrographically and showed aluminum, iron, and magnesium in the 0.1 to 0.05 percent range, barium in the 0.005 to 0.01 percent range, and manganese in the 0.0005 to 0.001 percent range. Results given by the mandelic acid precipitation method were selected for comparison with the spectrographic results because of the high purity of the precipitates. These comparisons are shown in table 1.

As a further check on the spectrographic results two samples were prepared to simulate the natural zircon (table 2). Preparation techniques similar to those used in preparing the standards were applied to the simulated samples including the addition of minor and trace elements. The percentage of zirconium added was varied in the simulated samples but remained constant in the standards. This step was for the purpose of checking the accuracy of the zirconium determinations when calculated mathematically using the hafnium and hafnium-zirconium ratio data. When a line produced by a major component is used as an internal standard, a variation in the percentage of this major component beyond certain limits can introduce error into the method. This effect was studied in the simulated samples where the zirconium content varied 7 percent. This amount of variation in the zirconium content of the zircon samples indicated an insignificant effect upon the accuracy of the

Table 1.--Comparisons in percent of chemical and spectrographic analysis for hafnium plus zirconium in zircon samples.

Sample no.	Hafnium + Zirconium		
	Spectrographic	Chemical	Difference
Z-55	46.5	43.89	+2.61
1-26B	51.3	48.54	+2.76
2-17A	51.6	48.69	+2.91
2-18B	49.4	49.06	+0.34
Z-6a	48.4	47.36	+1.04
4-33B	51.7	50.10	+1.60
		Average	+1.87

Table 2.--Comparisons of spectrographic and calculated percentages of hafnium and zirconium in simulated zircon samples.

Sample no.	Element	Added	Found	Ratio	Calculated	Difference Zr	Difference Hf
S-1	Zr	43.0			45.6	2.6	
	Hf	0.5	0.48	0.0105			-0.02
S-2	Zr	50.0			48.3	1.7	
	Hf	1.0	1.05	0.0216			+0.05

hafnium determinations (table 2).

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 24 exposures of a standard sample containing 1 percent hafnium and 50 percent zirconium, are shown in table 3. The greatest variation for hafnium was 0.11 percent in two observations and 0.09 in two observations; the other observations for hafnium are in a range from 0.02 to 0.06 percent, with an average spread of 0.04 percent. The greatest variation for the hafnium-zirconium ratio was 0.003 with an average difference of 0.002. The hafnium-zirconium ratios and the hafnium percentages were determined first, then the zirconium percentages were obtained indirectly by arithmetic, thus making use of the data already available. The greatest zirconium variation, as shown in table 3, was 3.6 percent, with an average variation of 1.9 percent. Other methods, such as X-ray fluorescence, would probably be more accurate for the zirconium determinations.

ACKNOWLEDGMENTS

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Table 3.--Reproducibility data on standard sample containing 1 percent hafnium and 50 percent zirconium.

Observation	Hf	Difference	Hf/Zr	Difference	Zr	Difference
1	0.89	-0.11	0.017	-0.003	52.3	+2.3
2	0.91	-0.09	0.017	-0.003	53.3	+3.3
3	0.94	-0.06	0.018	-0.002	52.2	+2.2
4	0.98	-0.02	0.019	-0.001	51.6	+1.6
5	1.00	0.00	0.020	0.000	50.0	0.0
6	1.00	0.00	0.020	0.000	50.0	0.0
7	0.98	-0.02	0.019	-0.001	51.6	+1.6
8	1.05	+0.05	0.022	+0.002	47.8	-2.2
9	0.98	-0.02	0.019	-0.001	51.6	+1.6
10	0.96	-0.04	0.018	-0.002	50.5	+0.5
11	0.95	-0.05	0.018	-0.002	52.6	+2.6
12	0.97	-0.03	0.018	-0.002	53.6	+3.6
13	0.97	-0.03	0.018	-0.002	53.6	+3.6
14	0.95	-0.05	0.018	-0.002	52.6	+2.6
15	0.96	-0.04	0.018	-0.002	53.3	+3.3
16	0.98	-0.02	0.019	-0.001	51.6	+1.6
17	1.05	-0.05	0.022	+0.002	47.8	-2.2
18	0.98	-0.02	0.019	-0.001	51.5	+1.5
19	1.00	0.00	0.020	0.000	50.0	0.0
20	1.00	0.00	0.020	0.000	50.0	0.0
21	0.98	-0.02	0.019	-0.001	51.5	+1.5
22	0.94	-0.06	0.018	-0.002	52.2	+2.2
23	0.91	-0.09	0.017	-0.003	53.4	+3.4
24	0.89	-0.11	0.017	-0.003	52.3	+2.3
Average	0.97	+0.04	0.019	+0.002	51.5	+1.9

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