

Artigo

Evaluation of Analytical Methods for Lead (Pb) (USEPA 3051) and Zinc (Zn) (HR-CS AAS) in Sediments**Brandelero, S. M.*; Miquelluti, D. J.; Campos, M. L.; Ferraz Neto, J.;
Moreira, M. A.***Rev. Virtual Quim.*, 2018, 10 (3), 518-528. Data de publicação na Web: 28 de junho de 2018<http://rvq.sbgq.org.br>**Avaliação de Métodos Analíticos de Pb (USEPA 3051) e de Zn (HR-CS AAS) em Sedimento**

Resumo: Diversas técnicas de análise podem ser utilizadas para determinar a concentração de metais no sedimento, como os métodos 3050, 3051 e 3052 da United States Environmental Protection Agency (USEPA). A leitura de amostras após a digestão pode ser realizada em espectrometria de absorção atômica de alta resolução de fonte contínua (HR-CS AAS), e pode ser aplicada a técnica de correção de fundo pelo algoritmo de mínimos quadrados (LSBC). O presente estudo teve por objetivo testar os tempos de digestão (5000 s, digestão um e 1800 s, digestão dois) pelo método 3051, na determinação de Pb e corrigir possíveis interferências espectrais na determinação de Zn em amostras de sedimento pela LSBC. A amostragem foi realizada no Rio Palmeiras, afluente do Rio Tubarão, SC, Brasil. As amostras foram digeridas em forno de micro-ondas e leituras em HR-CS AAS, com atomização em chama. Para Pb, realizaram-se as leituras das amostras digeridas das digestões um e dois, e para Zn, realizaram-se as leituras apenas da digestão dois, sem e com a LSBC. Observaram-se menores variações de temperatura e maiores taxas de recuperação de Pb na digestão dois. O uso da LSBC nas leituras do Zn possibilitou a obtenção de valores mais acurados.

Palavras-chave: Metais, Micro-ondas, Absorção atômica.

Abstract

A variety of analytical techniques may be used to determine the concentration of metals in sediment, such as methods numbers 3050, 3051 and 3052 of the United States Environmental Protection Agency (USEPA). The reading of samples after digestion can be carried out by high-resolution continuous source atomic absorption spectrometry (HR-CS AAS), and background correction technique can be applied by the squared minimums algorithm (LSBC). This study aims to test the digestion times (5000 s, for first digestion and 1800 s for second digestion) using the 3051 method, to determine the Pb level and correct possible spectral interferences in the determination of Zn in sediment samples by LSBC. Sampling was conducted in the Palmeiras River, a tributary of the River Tubarão, SC, Brazil. Samples were digested in microwave ovens and readings in HR-CS AAS with flaming atomization. Pb readings were found for the samples digested in number one and two digestions, and a Zn reading was found in only the second digestion, with and without LSBC. Minor variations in temperature were observed and higher Pb recovery rates were found in the second digestion. The use of LSBC in Zn readings made it possible to obtain more accurate values.

Keywords: Metals; Microwave; Atomic absorption.

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Evaluation of Analytical Methods for Lead (Pb) (USEPA 3051) and Zinc (Zn) (HR-CS AAS) in Sediments

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1. Introduction
2. Materials and methods
3. Results and discussion
4. Conclusions

1. Introduction

Chemical elements such as metals are present in the environment and their concentrations may be increased due to human activities in substances such as water, sediment and soil from the river bottom. In recent decades, the process of digestion of samples for quantification of metals using microwave ovens has been highlighted as a method of performing extractions from within a closed system. According to Chen and Ma¹, it is fast, safe, efficient and not susceptible to losses during the analytical process.

The selection of suitable analytical methods is essential for the accurate

quantification of a specific metal. To achieve this goal it is necessary to have some idea of the concentration in a given sample (expected concentration), with the use of certified reference materials necessary for the validation of analytical methods, thus ensuring the quality of data. According to the International Organization of Standardization (ISO)², reference samples have properties sufficiently well established to allow the calibration of an instrument, validate an analytical method and fix values for the material.

Various methods of analysis may be used to determine the concentration of metals in the sediment; methods contemplated by the United States Environmental Protection Agency (USEPA), such as 3050A³ and 3050B⁴

using digester blocks and nitric acid and/or hydrochloric acid; 3051⁵ and 3051A⁶ which utilize micro-waves, nitric acid and alternatively hydrochloric acid, and 3052⁷ which uses hydrofluoric acid as well as microwave ovens. For digestion methods 3050 and 3051 we considered the total quantity recovered and with 3052, the total digestion⁸. In certified sample analysis, method 3051 showed recoveries of 65% to 99% for Pb and 61% to 92% for Zn compared to values of 89% and 83% obtained by the 3052 method.⁹

The quantification of potentially available metals is emphasized for environmental impact studies, with the dissolution of silicates for pollutant detection not being necessary.⁸ In this case, the 3051 method is simple, low cost and highly efficient for the extraction of metals.^{10,11}

The addition of HF (hydrogen fluoride) to the mixture of acids has been shown to increase the efficiency of digestion; however, the corrosive power of this acid undermines the instruments under analysis.^{12,10} For Sastre¹³ there was no statistically significant difference between total digestions that used a mixture of acids compared to those in which only HNO₃ was used.

Pressure is also an important variable for the microwave digestion method; it is generated during the decomposition of the sample and must be controlled to avoid exceeding the maximum working value and furthermore the process is carried out safely and quickly. The actual pressure in the digestion tube is dependent on the rotor itself, the amount and type of acid used, the temperature and the size and composition of the sample. Also, we see that the reaction rate and the extraction efficiency increase with the temperature.¹²

The USEPA⁵ advocates a 900 s digestion time plus cooling time for the 3051 method. However, with the use of the 3051 method, heating times of 2160 s, 1440 s and 1500, gave recoveries of 103 %, 104 % and 102 % for Pb and 95 %, 101% and 79 % for Zn.¹⁴

The reading of samples after digestion can

be carried out in an atomic flame absorption spectroscopy (FAAS). In conventional instruments, a source of radiation for each specific element (source line) is usually used, which implies that only the rows of the element itself are emitted by the source. In high-resolution continuous source atomic absorption spectrometry (RH-CS AAS), unlike atomic absorption instruments with line sources (LS AAS), the concept of simultaneous double beam is utilized, which is possible due to the instrument's detector charge coupled device (CCD). The 200 pixels used for analytical purposes can be considered as independent detectors.¹⁵ Zn values greater than those certified through using conventional equipment, were obtained under examination.¹¹

With the HR-CS AAS it is possible to increase the spectral resolution and set the CCD detector, allowing the nature of the background absorption to become visible, and facilitating decisions to adequately correct them. The determination of Zn may be difficult in samples with high levels of Fe as the main line of Zn (213,856 nm) is severely overlapped by a secondary line of Fe (213,859 nm). However, there is another line of Fe, which is close enough (213,970 nm) to which the application of background correction by squared minimums (LSBC) is adequate.¹⁶ It is a fast, simple and efficient way, in situations where the interfering signal is significant compared to the analyzed substance. The principle of LSBC involves subtracting the original spectrum signals associated with a reference spectrum generated by one or more substances which simulate the background.¹⁷

In this context, the present study aimed to evaluate the effect of different digestion time periods using the 3051 method, to determine the level of Pb, and correct possible spectral interferences of Fe in the determination (reading) of Zn in HR-CS AAS on sample sediments.

2. Materials and methods

The study was conducted on sediment samples from the Palmeiras River, as part of the Tubarão Basin, in a coal mining region. Sampling was conducted at eight points on the sediment surface, about 15 cm deep, with the aid of a plastic shovel, and the points were distributed from upstream to downstream in the river. The samples were placed in pre-labeled plastic bags, with samples taken at three sampling moments, August 2012, January and May 2013.

The sediment samples were dried in an oven with air circulation, and strained and filtered through a 2 mm 10 mesh. Subsequently, these samples were ground in agate mortar and filtered through a 0.10 mm 10 mesh.

Digestion was performed in duplicate, according to the USEPA method 3051⁵, which considers the use of microwave and nitric acid. The sample size used was 0.25 g of pellet in 6 mL of HNO₃ 14 mol L⁻¹, pH < 2 (analytical reagent grade - P.A.). The time for this digestion was 5000 s (digestion I) and 1800s (digestion II), therefore the modification of the 3051 method was obtained using a longer digestion I. Samples were digested in a microwave oven model Multiwave 3000 / Synthos 3000, version 2.2, Anton Paar, Graz, Austria, with AP-Softprint¹⁸ software, with tube port (rotor) for 48 MF50-T48 positions, PFA Teflon tubes of 50 mL (capacity 25 mL) jackets for pipes with PEEK cover. The maximum operating conditions for temperature and pressure were 200 °C and 20 bar.

After digestion, the pellet samples were filtered through quantitative filter paper (slow filtration) and then washed with 10 mL of ultrapure water (Milli-Q®, electrical conductivity of approximately 1 s⁻¹ cm). Quantification of metals was carried out in triplicate, in a high resolution continuum source atomic absorption spectrometer (HR-CS AAS) with flamed atomization. It used

ContrAA Analytik Jena 700 equipment (Analytik Jena, Jena, Germany) equipped with a short arc lamp with 300W of xenon power (XBO 301 GLE, Berlin, Germany) as the continuous source. This has double monochromatic high-resolution Echelle grating, and a charge-coupled device detector (CCD) with 5 pm resolutions per pixel. The number of pixels used in the CCD to detect (s) line (s) of continuous source were 3 (central pixel ± 1). An acetylene flame/compressed air were used.

The wavelengths used for the readings were of 283 nm to 213 nm for Pb and Zn. Pb readings were made on digestion samples I and II, the Zn readings only from the digestion II sample.

Zn readings were performed with and without background correction by the algorithm of squared minimums (LSBC) with a correction filter aid for the permanent structures of the AspectCS software¹⁹ and as a background simulator, a standard Fe solution (SpecSol®) of 1.44 mol L⁻¹ HNO₃ was used. The analytical curves for the determination of Pb and Zn were obtained using ultrapure water (Milli-Q®), electrical conductivity of approximately 1 s⁻¹ cm) with respective patterns (SpecSol®) of the elements prepared in a solution of 0.72 mol L⁻¹ HNO₃. All the material was left in a 0.72 mol L⁻¹ HNO₃ solution for 24 hours, and then washed three times with distilled water and once with ultrapure water, before use.

The analytical curves for the determination of Pb and Zn were obtained using ultrapure water (Milli-Q®), electrical conductivity of approximately 1 s⁻¹ cm, with respective patterns (SpecSol®) of the elements. prepared in a 0,72 mol L⁻¹ solution of HNO₃. The points for the construction of the analytical curve were 0, 5, 10, 15 and 20 mg kg⁻¹ for Pb and 0, 0.4, 0.8, 1.2 and 1.6 mg kg⁻¹ for Zn, with triplicate reading and R² = 0.99, where necessary, dilution of the sample to be read. All material was left in a solution of 0.72 mol L⁻¹ HNO₃ for 24 hours, and then washed three times with distilled water and once with ultrapure water, prior to

use.

The reliability of the analytical methods was assessed using soil sample references certified by the National Institute of Standards and Technology (NIST). For the analysis in question, the soil sample SRM 2709th (San Joaquin) was used as a reference. Also the operating limits of detection (LDO) and the limits of operating quantification (LQO) were measured according to AspectCS software¹⁹

Data for Pb were subjected to variation analysis, considering the collection points as a random effect factor and samplings and digestion times as fixed effect factors. Zn data were submitted to variation analysis, considering the collection points as a random effect factor and the samplings and the presence / absence of LSBC correction as fixed effects factors. For verification of

normality and homogeneity of variance Shapiro-Wilk and Levene tests were used. Statistical analyzes were conducted with the use of SAS® software (Statistical Analysis System)²⁰ and R (R Core Team)²¹, considering a 5 % level of significance.

3. Results and discussion

In digestion I maximum conditions were 190 °C, 7 bar and 1200 W, while in the digestion II they were 180 °C, 4 bar and 1200 W. Variations in the amounts of temperature, pressure and power were observed in the conditions of the microwave oven as shown in Figure 1, digestion I (a) and digestion II (b).

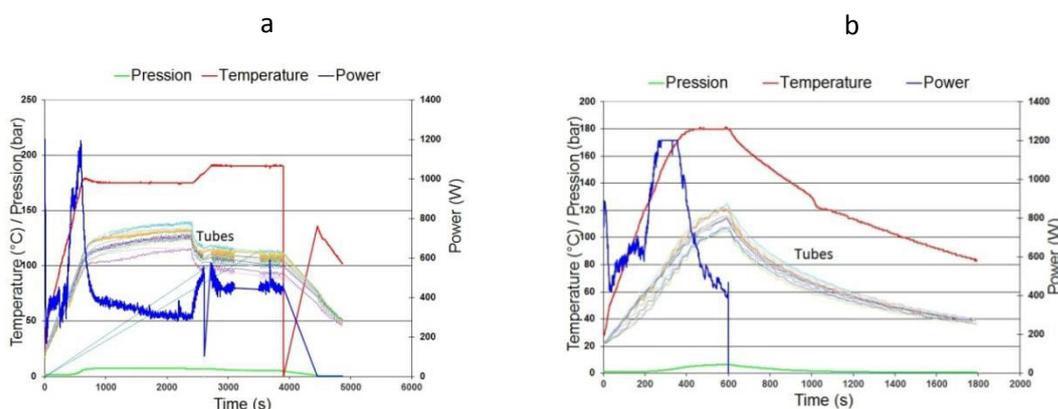


Figure 1. Behavior of digestion I (a) and digestion II (b) for temperature, pressure and power

Still in Figure 1, considering the samples (tubes), digestion I there was a gradual heating increase of 600 s reaching temperatures between 100 and 140 °C, lasting for 1700 s, 2700 s followed by cooling (heating time 38 minutes); digestion II occurred with a gradual heating increase for 600 s reaching temperatures between 100 and 125 °C, 1200 s followed by cooling (heating time 10 minutes). The USEPA⁵ advocates operating conditions for the 3051 method of a graded slope up to 300 s to reach 175 °C, remaining between 170 °C and 180 °C for 600 s, so the microwave oven

conditions occurring in digestion II were closer. Digestion II showed less variation in temperature. Roje²² observed that even when there is little variation in the applied digestion temperature; it affects the extraction efficiency of the elements.

The Pb concentrations found ($R^2 = 0.99$) in the two sediment digestions collected at different points and sampling times were different in digestions I and II ($P < 0.05$) for most of the sampling points, as per Table 1. The average concentrations of Pb in digestion II, were in general higher than those groups in digestion I, reaching 151 % variation. The

recovery of the reference sample (NIST SRM-2709th) in addition to the Limits Operating Detection (LOD) and Limit Operational Quantification Limits (LOQ) for Pb, are shown in Table 2.

Table 1. Average total concentrations and percentage change (Δ %) for Pb according to the type of digestion and the time of collection from the Palmeiras River sediments, SC

POINT	TIME	Pb (mg kg ⁻¹)		
		Digestion I*	Digestion II*	Δ %
1	AUG	17.69 b	30.20 a	70.72
1	JAN	22.76 b	28.79 a	26.49
1	MAY	18.40 b	9.61 a	-47.77
2	AUG	16.83 b	21.12 a	25.49
2	JAN	15.63 a	17.26 a	10.43
2	MAY	18.36 a	19.51 a	6.26
3	AUG	25.50 a	28.80 a	12.94
3	JAN	20.77 a	23.28 a	12.08
3	MAY	18.81 b	23.76 a	26.32
4	AUG	20.13 b	24.06 a	19.52
4	JAN	16.35 a	18.69 a	14.31
4	MAY	16.33 a	18.52 a	13.41
5	AUG	17.16 b	21.05 a	22.67
5	JAN	16.79 b	20.78 a	23.76
5	MAY	17.69 b	21.87 a	23.63
6	AUG	19.34 b	27.54 a	42.40
6	JAN	24.09 b	48.57 a	101.62
6	MAY	19.79 b	26.96 a	36.23
7	AUG	16.29 b	19.31 a	18.54
7	JAN	18.85 b	25.72 a	36.45
7	MAY	10.53 b	13.65 a	29.63
8	AUG	6.20 b	14.23 a	129.52
8	JAN	10.45 b	14.04 a	34.35
8	MAY	5.53 b	13.89 a	151.18

Averages followed by the same letter (in the row), did not differ statistically by the F test ($P < 0.05$).

* The time for this digestion was 5000 s (digestion I) and 1800s (digestion II)

Table 2. Certified values and recoveries of Sample Reference NIST 2709a, limits of detection and operational quantification for Pb in digestions I and II

ELEMENT	NIST 2709a CERTIFIED (mg kg ⁻¹)	RECOVERY (%)	LOD*(mg kg ⁻¹)	LOQ*(mg kg ⁻¹)
Digestion I				
Pb	17.30	49	0.067	0.202
Digestion II				
Pb	17.30	76	0.013	0.041

*Limits Operating Detection (LOD) and Limit Operational Quantification (LOQ).

In Table 2 it can be seen that the digestion II recovery values are higher than those obtained in the Pb digestion I. The recovery obtained in the digestion II, using the 3051 method is higher than that for the certified 3050B method (block digester) (53 %), and also the recovery as shown by Chen and Ma⁹ (65 %), which had used the same reference sample (NIST SRM 2709th) and the 3051 method.

Higher recovery rates to those found in this study were observed in other studies. In operating temperature conditions of up to 230 °C, adopting a gradient of 1200 s, and maintained and cooled in two equal time periods, they achieved recovery rates of 99 % for Pb, with the 3051 method and of between 90 to 97 % with regia water (nitro hydrochloric acid) and of 105 % and 87 % using full digestion.^{22,23} With operating temperatures of up to 200 °C, digestion in 1500 s, added cooling time of 900 s, 97 % and 98 % recovery rates were achieved with regia water.²⁴ Working with temperatures of up to 300 °C with complete and total digestion time of from 2160 s to 2940 s digestion, we obtained 90-102 % recovery.²⁵ Hewitt and Reynolds²⁶, under similar conditions to the present study, obtained recovery rates from 67 % to 104 %, while Sanjeevani *et al.*²⁷ found 92 % Pb. Using a heating gradient of 600 s to 165 °C followed by a gradient of 180 s to 175 °C and temperature maintained for 600 s Sakan *et al.*²⁸ showed a 90 % recovery. Adopting a 300 s graduated heating increase,

in which a temperature of 175 ± 5 °C was reached, and maintained for 300 s, KRISHNA *et al.*¹⁰ obtained up to 78 % Pb recovery.

Other authors tested digestion times of 900 s and 1500 s, and detected no significant differences, indicating that the time of 900 s is sufficient to complete digestion.¹² Comparing those digestion II times, in which higher digestion times were used, for example, a total time of 2340 s digestion, 82 % to 89 % Pb was recovered.²⁹ Therefore, it can be considered that longer digestion times do not necessarily imply a greater recovery of elements.

Studies using the method of total digestion with 2100 s duration, recovered 95 % to 172 % Pb.²⁶ With a total time of 2340 s digestion, 85 % to 101 % was achieved.²⁹ Working with 5460 s digestion, they recovered up to 107 %.¹³ Using a 360 s gradual heat increase with a temperature of 180 ± 5 °C, and held for 600 s, they recovered 101 %.¹⁰ These values are higher in general than those achieved in this study.

In digestion II there was a higher extraction of Pb, in relation to digestion I. Therefore, the increase of the digestion time, considering the experimental conditions of the microwave oven used, did not provide a higher extraction of Pb.

The atomic absorption spectra for reading Zn with and without LSBC correction are presented as Figure 2 (a) and (b).

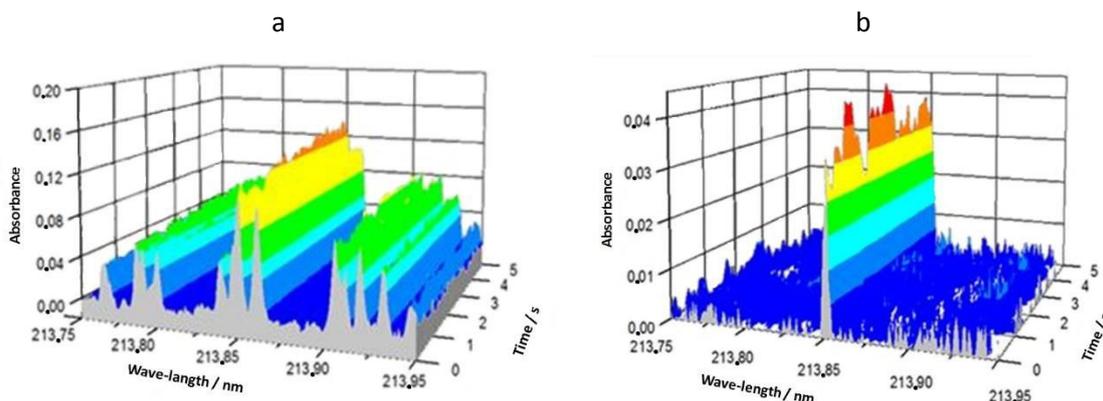


Figure 2. Atomic absorption spectra for Zn without (a) and with (b) LSBC correction

The use of the HR-CS AAS flame atomization enabled the identification of and the correct interferences in the spectral region of the primary Zn wavelength. The spectral interferences are mainly caused by Fe, therefore, using the standard 850 mg L⁻¹ of Fe in association with squared minimums background correction (LSBC) allowed for greater accuracy in determining the concentration of Zn in the sediment.

The mean concentrations of Zn ($R^2 = 0.99$) in sediment samples, in three different moments and from different sampling points, as expected, were lower in readings which used squared minimums background correction (LSBC), i.e., eliminating the interference of Fe as in Table 3. The maximum concentration was 947.90 mg kg⁻¹ and a minimum of 122.76 mg kg⁻¹ with no background correction, whereas with

background correction, these concentrations were 176.36 mg kg⁻¹ and 20.26 mg kg⁻¹, in the sediment samples. The concentrations decreased by 80-89 % when squared minimums background correction was carried out, eliminating possible spectral interference for Fe in the Zn reading.

Recoveries found in the sample (NIST SRM-2709th) showed readings of 555 % without LSBC correction and 72 % with the correction (LSBC), which was similar to the certified value of 77 % for the 3050B method. Operating limits of detection (LDO) and operating quantification (LQO) were respectively 0.15 mg kg⁻¹ and 0.45 mg kg⁻¹ for reading without correction and 0.04 mg kg⁻¹ and 0.13 mg kg⁻¹ for reading with background correction. Therefore, Monica *et al.*¹¹, who did not use the correction, obtained Zn recovery values of around 225 %.

Table 3. Average concentrations of Zn sediment samples, in three time periods and sampling points, with and without background correction (LSBC) and (Δ %) with the correction

POINT	TIME	Zn (mg kg ⁻¹)		
		with/LSBC	without/LSBC	Δ %
1	AUG	176.36 b	947.90 a	-81.40
1	JAN	131.27 b	915.14 a	-85.66
1	MAY	150.64 b	811.91 a	-81.45
2	AUG	58.63 b	405.91 a	-85.56

2	JAN	58.50 b	338.39 a	-82.71
2	MAY	72.22 b	501.23 a	-85.59
3	AUG	73.82 b	518.78 a	-85.77
3	JAN	37.82 b	319.53 a	-88.16
3	MAY	71.65 b	503.17 a	-85.76
4	AUG	38.21 b	297.13 a	-87.14
4	JAN	32.79 b	227.87 a	-85.61
4	MAY	33.61 b	261.16 a	-87.13
5	AUG	30.19 b	217.86 a	-86.14
5	JAN	35.50 b	226.07 a	-84.30
5	MAY	32.02 b	232.15 a	-86.21
6	AUG	43.36 b	278.53 a	-84.43
6	JAN	38.58 b	195.82 a	-80.30
6	MAY	39.19 b	249.36 a	-84.28
7	AUG	53.62 b	407.08 a	-86.83
7	JAN	26.63 b	250.76 a	-89.38
7	MAY	20.26 b	152.12 a	-86.68
8	AUG	29.90 b	173.56 a	-82.77
8	JAN	26.73 b	179.30 a	-85.09
8	MAY	20.93 b	122.76 a	-82.95

Averages followed by the same letter (in the row), did not differ statistically by the F test (P <0.05)

4. Conclusions

The smallest change in oven conditions and in the samples from the procedures for digestion II increased the extraction of Pb in comparison to digestion I, with mean concentrations and recovery values generally greater. Therefore, increasing the digestion time, considering the experimental conditions of the microwave oven used did not provide greater extraction of Pb.

The use of squared minimums background correction (LSBC) resulted in a more accurate reading for Zn, with the average concentrations and recovery values decreasing by 80-89 %.

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