

Statistical optimization of surfactant assisted dispersive liquid-liquid microextraction for trace mercury determination by GF-AAS

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Received June 26, 2015; Revised September 10, 2015

A new method of surfactant assisted dispersive liquid-liquid microextraction prior to graphite furnace atomic absorption spectroscopy (GF-AAS) has been developed for determination of trace amounts of mercury in aqueous solutions. In this method, Triton X-114 (TX-114), a non-ionic surfactant, compared with DLLME, was substituted as disperser solvent and emulsifier agent that could afford effective emulsification and make the extraction comparatively greener.

The effects of different experimental factors on the extraction was examined using two experimental design methods; a screening design to identify more effective parameters and a central composite design at five levels of the operating parameters to find out optimum values.

Under the optimal conditions, the limit of detection (LOD) for mercury was $0.023 \mu\text{g.L}^{-1}$, with enhancement factor (EF) of 125 and the relative standard deviation (RSD) of 8.1% ($n=5$, $C=1.0 \mu\text{g.L}^{-1}$).

The proposed method was applied for preconcentration and determination of mercury in different aqueous samples and the recoveries for the spiked samples were in the range of 95 – 106%.

Keywords: Surfactant assisted dispersive liquid-liquid microextraction, Triton X-114, Mercury, Experimental design

INTRODUCTION

Mercury could be released to the nature from two major sources, weathering of rocks that contain Hg and industrial activities; also using mercury-containing fungicides may lead to releasing Hg to the environment. Another and major source of Hg contamination includes waste incinerators and coal-fired utilities [1].

Rise in environmental mercury occurred in condition that this element is very harmful for health. According to the researches, mercury pollutants could affect many different areas of the brain and its associated functions, resulting in a variety of symptoms. These include personality changes (shyness, irritability, and nervousness), changes in vision (constriction of the visual field), tremors, loss of sensation, deafness, muscle incoordination and difficulties with memory [2].

Mercury compounds also have been introduced by the US Environmental Protection Agency as possible human carcinogens. Therefore, the development of rapid and accurate determination methods for monitoring the levels of mercury in natural waters is absolutely necessary [3].

Regardless of good developments in the modern analytical instruments, direct trace determination of

analytes at low concentrations is often a difficulty for analytical chemists and so a sample-preparation step is necessary [4,5].

Convention sample preconcentration and preparation methods such as solid phase extraction (SPE) and liquid-liquid extraction (LLE) are time consuming, laborious and need a large amount of organic solvents.

In recent years, many researchers have focused on these methods to provide alternative pre ecological solvent-free extraction methods or techniques employing a minimal amount of solvents.

LLE is one of the oldest extraction techniques used most frequently in the case of aqueous samples with complex matrix composition [6].

First attempts to miniaturized LLE methods lead to introducing liquid phase microextraction (LPME) and then dispersive liquid- liquid microextraction (DLLME) methods [7]. The latter is basically consists of a proper mixture of disperser and extraction solvent that is injected into the aqueous sample containing analyte(s) rapidly. The cloudy solution is formed as a result of the formation of fine droplets of extraction and disperser solvent in the solution. Finally, the cloudy solution is centrifuged and small sedimented phase containing extracted analyte(s) is analyzed by appropriate analytical instruments [8].

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DLLME is a low cost, fast and efficient extraction method but not completely environmental friendly. The main disadvantage of DLLME is using relatively high volume of disperser solvents (in ml range) such as acetonitrile or methanol. Usual disperser solvent are harmful and environmentally unfriendly. Another disadvantage is decreasing extraction efficiency because of increasing analyte solubility in the presence of a disperser solvent [9,10].

Among the efforts made to solve these problems and to develop miniaturized extracting method, one has led to surfactant-assisted dispersive liquid-liquid microextraction (SA-DLLME) [11-13]. In this method, surfactant was used as an environmental friendly emulsifier. Surfactants are surface (or interface) active chemicals that have both hydrophobic and hydrophilic parts, and are soluble in organic solvents and water. Because of particular properties, these compounds are considered good choices as disperser solvents in DLLME [14].

In the present study, SA-DLLME method for determination of Hg contamination in trace levels in an aqueous sample has been developed.

The first step in Hg²⁺ extraction into organic solvent from the aqueous phase is forming a suitable complex with acceptable hydrophobicity. Diethyldithiocarbamate (DDTC), an appreciate chelating agent, was used in this study to extract Hg ions from aqueous solutions.

DDTC can form complexes with many metallic ions under suitable pH to extract metal ions into appreciate organic solvents. It is a common chelating agent which forms stable complexes with transition metals [15,16].

In SA-DLLME, a surfactant is used as a substitute of traditional disperser solvents in DLLME. The Triton X-114 (TX-114) is the most widely used surfactant that has been used in surfactant-assisted DLLME method [17,18] and was applied in this study. TX-114 is a Non-ionic surfactant with good emulsification properties which makes the extraction relatively greener.

A few microliters of an organic solvent containing suitable amount of TX-114 were used to extract the Hg from water samples.

Some affecting parameters on extraction process that must be optimized are as follows: volume of extraction solvent, concentration of chelating agent, time of extraction, pH, sample volume and salting out effect. One method for obtaining the best condition is using an experimental design method intended to: (1) Investigating the effect of different factors can affect enrichment factor in the extraction procedure. (2) Identifying the factors that have

higher impact on the extraction results. (3) Obtaining a better insight about the method that would help us to find optimized conditions considering the interactions between factors. These steps have been done by Plackett Burman [19,20] design, central composite design [21,22] and response surface methods [23], respectively.

The extracted analytes were determined by graphite furnace atomic absorption spectroscopy (GF-AAS). The analytical efficiency and possible application of the method in real water sample analysis were also investigated.

EXPERIMENTAL

Material and methods

Reagents and chemicals. All used reagents were of analytical grade purity purchased from Merck (Germany). Stock solution of mercury (1000 mgL⁻¹) was prepared by dissolving the appropriate amount of HgCl₂ (Merck, Darmstadt, Germany). Working standard solutions were prepared daily by appropriate dilutions of the standard stock solution. Working standard solutions were prepared daily by stepwise diluting of stock standard solutions.

Diethyldithiocarbamate (DDTC) was solution prepared by dissolving suitable amount of the compound (Shanghai Reagent Factory, Shanghai, China) in 100 ml of deionized water.

Apparatus. An atomic absorption spectrometer (Unicam AA929) equipped with continuous source background correction (deuterium lamp) and graphite furnace atomizer (GF90) were employed. Hollow cathode lamps were utilized as the radiation source for each element. Instrumental parameters for mercury are shown in Table 1. The pH was measured by using a pH meter (Metrohm 691 pH meter).

Table 1: Instrumental parameters for Mercury

Instrumental parameters	Mercury		
Wavelength (nm)	253.7		
Bandwidth	0.5		
Atomizer type	Electrographite		
Injected sample volume (μl)	20		
Background correction	D ₂		
Furnace heating program			
Step	Temperature Hg (°C)	Time (Sec)	Ramp (°C.S ⁻¹)
Drying	120	30	10
Pyrolysis	500	10	50
Atomization	1400	3	0
Cleaning	1900	6	0

DLLME Procedure. 10 ml of sample solution after PH adjustment was placed in conical test tube. Then appreciate concentration of ligand (DDTC) was

transferred into the vessel leading to form hydrophobic complex. Then, optimal amounts of surfactant (TX-140) were added into the solution and 180 μL of extractant (CCl_4) was injected rapidly into the solution using a syringe. After the injection and shaking manually for 1 min, the solution became turbid because of the presence of emulsifier (surfactant) and so CCl_4 was dispersed into fine droplets to extract the analytes. After this step, Cloudy solution was centrifuged to remove sedimented extraction phase at the bottom of conical test tube and finally it was placed in the graphite furnace cuvette using 20 μl Hamilton syringe for AAS analyses.

RESULT AND DISCUSSION

Optimization Step

Some factors had effects on determination of Hg by SA-DLLME and should be optimized. Therefore, enrichment factor (EF) was chosen as an analytical response under different conditions. The enrichment factor as a response is defined in Eq. (1):

$$EF = C_{\text{sed}} / C_0 \quad (1)$$

where EF is enrichment factor; C_{sed} and C_0 are analyte concentration in sedimented phase and primary analyte concentration in aqueous phase, respectively. C_{sed} was obtained from conventional LLE-ETAAS calibration curve (extraction condition: 10 ml of standard water sample, ligand concentration of 0.024M, 10 ml CCl_4 and pH at 5.06).

Extraction solvent optimization

The first step in SA-DLLME is finding a suitable extraction solvent. The extraction solvent must meet some conditions such as low solubility in water and low volatility, high capacity for analyte extraction and having density more than water. Generally extraction solvent conditions in SA-DLLME are very similar to conventional DLLME.

Three solvents that have these properties including CH_2Cl_2 , CHCl_3 and CCl_4 were examined. The highest enrichment factor at same condition was obtained for CCl_4 , so CCl_4 was chosen as extraction solvent.

Experimental design

Some factors affect SA-DLLME and should be optimized, such as extraction solvent volume (A), ionic strength (B), pH (C), concentration of surfactant (D), extraction time (E), and ligand concentration (F).

Optimization of these several factors requires a lot of experiments and it is a time-consuming and costly procedure. A screening experimental design method called Plackett Burman was used to find

main effects with significant influence on resonance. After choosing significant factors, a central composite design (CCD) combined with response surface method (RSM) was used to derived response surface equation and to find optimized values for each factor.

Plackett Burman Design

A Plackett Burman design containing 12 runs was used to determined significant factors. Low and high levels for all factors were selected based on preliminary experiments. In order to eliminate nuisance and extraneous variables, these 12 runs were carried out randomly and after that, the ANOVA results were estimated for determining main effects.

Plackett Burman design values for each parameter in coded and uncoded values are shown in Table 2.

Table 2. Two level Plackett Burman design values

Parameters	Low (-1)	High (+1)
extraction solvent volume	50 μL	250 μL
ionic strength	5mmol/L	100mmol/L
Ph	3	9
concentration of surfactant	0.01 %v/v	0.05% v/v
extraction time	2 min	5 min
ligand concentration	0.01M	0.1M

Pareto chart of the studied variables has been obtained from screening experiment and are shown in Fig 1. The normalized effect of each variable is shown by horizontal bars and vertical line at 95% confidence level judges the effects that are statistically noteworthy.

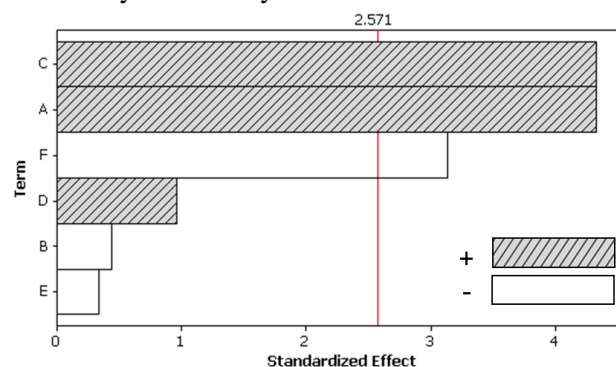


Fig. 1: Standardized ($P = 0.05$) Pareto chart, representing the estimated the most effective parameters, extraction solvent volume (A), ionic strength (B), pH (C), concentration of surfactant (D), extraction time (E), and ligand concentration (F).

Results indicate that the volume of extraction solvent (A), pH (C) and ligand concentration (F) were the most significant variables with noteworthy effects on the RF which were evaluated using CCD

for further assessment. Ionic strength (B) extraction time (E) and concentration of surfactant (D) were negligible parameters. The values of B and E were fixed at up level for further experiments because of their positive effects on extraction process. Commonly in DLLME experiments the extraction time (E) has no effect on extraction efficiency. It has been illustrated that due to the very large contact surface between the fine drops of extraction solvent and aqueous phase, DLLME process is a fast process. As it's shown here this parameter has positive and also unimportant effect on extraction process. Ionic strength (B) also was studied in 5 and 100 mmol/L of NaCl showing a positive negligible effect. Concentration of surfactant (D) was fixed at lower level because of their negative effect according to Pareto chart.

Considering the result of Plackett Burman design, three variables were fixed at suitable values (extraction time of 5 minutes, salt addition of 100 mmol/L of NaCl and surfactant concentration of 0.01% v/v of TX-114)

These factors had no significant effect on the ER and thus were eliminated for further studies by CCD.

Central composite design

According to screening design results pH(x₁), extraction solvent volume (x₂) and Ligand concentration(x₃) are effective variables on extraction results by SA-DLLME and should be optimized by a multivariate experimental design method.

A central composite design followed by response surface methodology was used to optimize the SA-DLLME process of mercury extraction. The CCD matrix with 3 independent variables (factor), N (number of experiments) = 20 and three repeats, r =4 was applied for model development.

The design matrix in coded and uncoded values, as well as the responses obtained from 20 experiments of a solution containing 1 µg.L⁻¹ of mercury have been shown in Table 3 and Table 4.

Table 3: The variables and values used for central composite design (CCD)

Variable name	Coded variable				
	-2	-1	0	1	2
Ph	3	4	5	6	7
extraction solvent volume	100	150	200	250	300
Ligand concentration	0.01	0.02	0.03	0.04	0.05

(mol/L)

Table 4: List of experiments in the CCD for model optimization (coded values) and the responses

Design points	Factors levels			Response
	F1	F2	F3	Enrichment factor
1	0	2	0	55.6
2	0	0	0	117.2
3	0	0	2	49.5
4	-2	0	0	51.8
5	2	0	0	45.2
6	-1	1	1	57.6
7	-1	-1	-1	99.1
8	0	0	0	119.0
9	0	0	-2	106.5
10	0	0	0	118.1
11	1	-1	1	74.2
12	1	1	-1	95.8
13	1	1	1	44.6
14	0	0	0	118.1
15	0	0	0	117.9
16	1	-1	-1	105.3
17	-1	1	-1	82.2
18	0	0	0	116.9
19	-1	-1	1	90.8
20	0	-2	0	101.4

Analysis Of Variance (ANOVA) test has been done on the obtained results. The ANOVA results (Table 5) are used to evaluate model suitability and adequacy of the fitted model and also to select suitable model terms.

The value of the adjusted R² = 0.9991 shows that this model has good predictive ability and there is acceptable match between predicted and experimental values.

The Model F-value of 2472.41 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise. Values of "Prob > F" less than 0.05 indicate that the model terms are significant. In this case x₁, x₂, x₃, x₁x₂, x₁x₃, x₂x₃, x₁², x₂², x₃² are significant model terms. Values greater than 0.05 indicate that the model terms are not significant. The "Lack of Fit F-value" of 1.44 implies that the Lack of Fit is not significant relative to the pure error. There is a 34.91% chance that a "Lack of Fit F-value" this large could occur due to noise. Non-significant lack of fit is good because we wish the model to fit.

Table 5: ANOVA results for CCD model

	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	9	15064.9	15064.9	1673.88	2472.41	0.000
Linear	3	5359.4	5359.4	1786.46	2638.71	0.000
x ₁	1	33.1	33.1	33.06	48.84	0.000
x ₂	1	2043.0	2043.0	2043.04	3017.68	0.000
x ₃	1	3283.3	3283.3	3283.29	4849.60	0.000
Square	3	9219.7	9219.7	3073.23	4539.33	0.000
(x ₁) ²	1	5193.2	5193.2	5193.23	7523.03	0.000
(x ₂) ²	1	1550.9	1550.9	1550.90	2413.60	0.000
(x ₃) ²	1	2475.6	2475.6	2475.58	3656.57	0.000
Interaction	3	485.8	485.8	161.93	239.18	0.000
x ₁ x ₂	1	15.1	15.1	15.12	22.34	0.001
x ₁ x ₃	1	305.0	305.0	305.04	450.57	0.000
x ₂ x ₃	1	165.6	165.6	165.62	244.63	0.000
Residual Error	10	6.8	6.8	0.68		
Lack-of-Fit	5	4.0	4.0	0.80	1.44	0.349
pure Error	5	2.8	2.8	0.55		
Total	19	15071.6				

The following equation was obtained for the response relating to x₁, x₂ and x₃:

$$y = 117.95 - 1.43x_1 - 11.30x_2 - 14.32x_3 - 17.29(x_1)^2 - 9.79(x_2)^2 - 9.92(x_3)^2 + 1.37x_1x_2 - 6.17x_1x_3 - 4.55x_2x_3$$

The optimum values were obtained by graphical analysis of response surface plots (Fig. 2). The response surface is a graph of a response as a function of effective factors. This model was optimized with respect to maximum signal that is proportional to 180 µl of extraction solvent volume and ligand concentration of 0.024M at pH 5.06. These optimized values were used for determination of mercury in the following experiments.

Performance of the SA-DLLME for mercury determination

The analytical efficiency of the proposed method was evaluated by determining the limit of detection, linear dynamic range and relative standard deviation (RSD).

The LOD was calculated as 3s_b/a where s_b is the standard deviation of the blank signal and "a" is the slope of calibration curve.

To evaluate these parameters, a series of solutions at 12 different concentration ranging from 0 to 3 µg.L⁻¹ were prepared.

Linearity was observed over the range of 0.08 to 2 µg/L with an acceptable correlation coefficient value. LOD value for mercury determination was obtained 0.023 µg/L and relative standard deviation (RSD) was 8.1%.

Results of proposed method compared with other published method are summarized in Table 6. It has been obviously concluded that this method is comparable with other published method and the

extraction time of this method is shorter than other extraction methods.

Table 6: Results of proposed method in compare with other published method

Method	Sample volume (ml)	EF	RSD	LOD (µg L-1)	Ref.
LLE-CV-AAS	1000	-	1.2	0.01	24
SPE-CV-AAS	250-400	300	0.8-1.7	0.01	25
LLE-FI-CV-AAS	20	36	2.8	0.0023	26
DLLME-CV-AAS	10	310	4	0.03	27
CPE- UV-VIS	50	6	4.8	14	28
SPE- UV-VIS	1000	100	2.5	4	29
SPE- UV-VIS	100	50	1.6	15	30
DLLME- UV-VIS	10	18.6	1.7	3.9	2
DLLME-HPLC-DA D	5	107	4.1-7.3	0.32	31
HF-LPME-ETV-IC P-MS	2.5	73	6.1	0.0048	16
SA-DLLME-GF-AAS	10	125	8.1	0.023	this work

The effect of foreign ions on Hg²⁺ determination by the proposed method was studied in the presence of common metal ions such as Na⁺, K⁺, Mg²⁺, Ca²⁺, Al³⁺, Cu²⁺ and Fe³⁺. For this reason, solutions containing 1 µg.L⁻¹ of Hg²⁺ and different concentration of foreign ions were prepared. The amount of these ions that would be tolerated without interference effects were examined and are demonstrated in Table 7. The results showed that the presence of large concentration of these common ions in water samples had no considerable effect on Hg determination by proposed SA-DLLME.

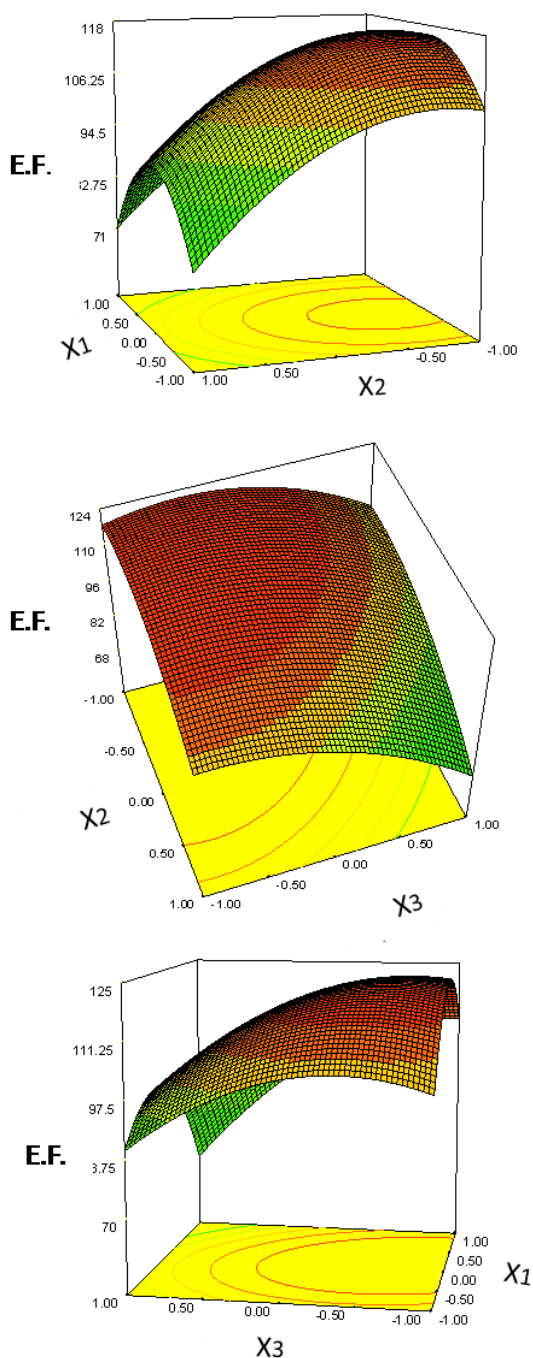


Fig. 2: Three surface plots that can be explained the optimal condition

Table 7: Tolerance limit of some coexisting ion (results within 10% error)

Ion	Tolerance limit $C_{ion}/C_{Analyte}$
Na	160000
K+	140000
Mg ²⁺	40000
Ca ²⁺	40000
Cu ²⁺	1400
Fe ³⁺	1000
Al ³⁺	4000

Real samples

The proposed SA-DLLME method was applied for Hg determination in water sample. In condition in which there is no standard reference with certified content as a target analyte, recovery study can be used as an alternative method for validation studies [24]. Tap and river water sample were collected as real samples. Kashan tap water was collected from our lab in Kashan University (Kashan, Iran). The river water sample was collected from Zayanderud River (Isfahan, Iran).

The recovery percentage was calculated by equation (3) where m_s and m_e are total amount of analyte and extracted amount into extraction solvent, respectively.

Also C_s , C_e , V_s and V_e are initial concentration of analyte in aqueous sample, concentration of analyte in extractant, volume of sample solution and volume of extraction solvent, respectively. C_e was obtained from calibration graph of Hg²⁺ complex using GF-AAS results.

$$R\% = \frac{m_e}{m_s} \times 100 = \frac{C_e V_e}{C_s V_s} \times 100 \quad (3)$$

Real sample were filtered by Millipore Membranes and then were extracted by the proposed method. Hg residues were found in the tap and river water samples at the concentration of 0.6 and 1.2 µg/L, respectively. The Percentage of Recoveries where standard solution of Hg was added at two different levels (0.5 and 1 µg/L) was also investigated and results are listed in Table 8. Results show that the recoveries for the spiked samples are within a satisfactory range (95 to 106 %) and so the proposed method is applicable for Hg preconcentration and determination in water samples.

In SA-DLLME a surfactant was used as a substitution for traditional disperser solvents in DLLME. The Triton X-114 is the most widely used surfactant that has been used in surfactant-assisted DLLME method and was applied in this study. TX-114 is a non-ionic surfactant with good emulsification properties which makes the extraction relatively greener.

CONCLUSION

In this paper, a new, reliable and disperser solvent free method based on SADLLME using DDTC chelating agent combined with GF-AAS was developed for mercury analysis in aqueous samples.

The method was fully optimized by screening design and multivariate methodology and it has been demonstrated that these are useful methods which enable us to determine significant variables and also

Table 8: Analytical results (mean \pm SD, n = 3) for trace Hg, in real water samples ($\mu\text{g/L}$)

Sample	Tap Water			River Water		
	Added ($\mu\text{g/L}$)	Determination ($\mu\text{g/L}$)	Recovery (%)	Added ($\mu\text{g/L}$)	Determination ($\mu\text{g/L}$)	Recovery (%)
Hg	0	0.60 \pm 0.08		0	1.2 \pm 0.07	
	0.5	1.05 \pm 0.07	95	0.5	1.65 \pm 0.07	103
	1	1.64 \pm 0.06	103	1	2.33 \pm 0.05	106

to evaluate the interaction of variables and determining the correct optimization.

The established method also was applied for the determination of mercury in some real water samples with satisfactory analytical results.

Some considerable features of this method include low cost and matrix effect, good extraction efficiency and recovery, more environmental friendly method compared with DLLME, because of the absence of organic disperser solvent, and also acceptable sensitivity and precision.

Acknowledgement. Authors are grateful to University of Kashan for supporting this work by Grant NO. 463609/1.

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