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Original Article

Study on Determination of Tin, Silver, Molybdenum and Lead in High-Tin Geochemical Samples by CCD-I Plane Grating Electric Arc Direct Reading Emission Spectrometer

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Abstract:
A method for the determination of tin, silver, molybdenum and lead in high-tin geochemical samples by CCD-I plana grating electric arc direct reading emission spectrometer was established by selecting national-level synthetic silicate spectral analytical standards and ore standards for plotting the calibration curves, and germanium was used as the internal standard element to choose the appropriate analytical line pairs. The detection limits of the method were 0.129μg/g and the range of determination was 0.129~1700μg/g for tin; 0.01μg/g and the range of determination was 0.01~10μg/g for silver; 0.085μg/g and the range of determination was 0.085~100μg/g for molybdenum; 0.875μg/g and the range of determination was 0.875~1000μg/g for lead. the relative standard deviation (RSD,n=12) was in the range of 4.98%~8.96%, the accuracy (|ΔlogC|) was less than 0.1 respectively. The measured values were consistent with the recommended values.This method can simultaneously determine the content of Sn,Ag,Mo,and Pb in high-tin geochemical samples without dilution,thereby improving the accuracy and precision of the analytical results and meeting the requirements of quality management in geological and mineral laboratories.

Keywords : CCD-I plana grating electric arc direct reading emission spectrometer; high-tin geochemical samples; tin; silver; molybdenum; lead

Introduction

In the field of geological exploration and mineral resources investigation and evaluation, rapid and accurate determination of tin, silver, molybdenum, lead and other elements in geochemical samples is of great significance to the evaluation of mineral resources and geoscientific research.For the determination of tin, silver, molybdenum and lead, most of the workers tend to use the classical arc direct reading emission spectrometry (DREES) method[1-5], in which the upper limit of tin determination is only 100 μg/g. This method is widely adopted due to its advantages of easy operation, low cost and fast analytical speed.However, during the actual sample analysis, sometimes the tin content exceeds this upper limit by tens of times, which leads to the occurrence of selfabsorption of the spectral line, which affects the intensity of the spectral line or makes the standard curve deviate seriously,thus affecting the accuracy of the analytical results [6]. Traditional analytical methods usually use matrix modifiers or diluents to dilute the high content of tin into the measurable range, but due to the uncertainty of the dilution multiplicity,the homogeneity of the dilution mixing, and the tediousness of the operation, this method does not achieve efficient and satisfactory results[7].

Although some literature data exists on the use of alkali fusion treatment of samples, atomic fluorescence method[8], and ICP-AES method[9-10] for the determination of high tin content in samples, these methods suffer from the adverse effects of high alkali fusion salts on the determination results,as well as the cumbersome

operation process and high analytical cost. Currently, methods for the determination of single elements with high tin content by arc direct reading emission spectrometry have been reported[7,11-13], but few studies have been reported for the simultaneous determination of multiple elements such as tin, silver, molybdenum, lead, etc., in high-tin geochemical samples.

The aim of this study is to select reasonable mixing ratios of sample,substrate,spectral buffer,and grinding and mixing conditions,as well as suitable internal standard elements and analytical line pairs, to propose a method based on CCD-I plana grating electric arc direct reading emission spectrometer.This method aims to overcome the shortcomings of traditional analytical methods, increase the upper limit of tin determination,improve the accuracy and precision,and enable accurate determination of tin,silver,molybdenum,and lead in high-tin geochemical samples.The method is reliable and practical,providing a technical reference for the determination of Sn,Ag,Mo,and Pb in high-tin geochemical samples.

2 Experimental Component

2.1. Instruments and Materials

CCD-I plane grating electric arc direct reading emission spectrometer. XZJ-54 vibration stirrer, small agate beads (diameter 5mm). BSA 124S electronic analytical balance. DHG-9024 blast drying oven. agate mortar.

Graphite electrode:spectroscopically pure graphite electrode,diameter Φ4mm on the electrode for the cylindrical cone. the lower electrode for the fine-necked cup, aperture diameter of 3.8mm, hole depth of 4mm, wall thickness of 0.6mm, the diameter of the thin neck of 3mm, neck length of 4mm, the symmetry of each side of the opening of a diameter of 1mm small hole.

2.2. Reagent and Standard Series

Spectral buffer: $mK_2S_2O_7$:mNaF:$mA1_2O_3$:m toner= 22:20:44:14 containing 0.007% mass fraction of GeO_2 as internal standard, (developed by the Institute of Geophysical and Geochemical Exploration, Chinese Academy of Geological Sciences).

2% Sucrose ethanol solution:weigh 4g of sucrose, dissolve it in 100mL ofethanol and 100mL of water,and mix well.

National level synthetic silicate spectral analysis s tandard material series: substrate (GSES I),GSES I-1~GSES I-11. National level geochemical stand ard material:GBW07406(soil standard sample),G BW07980(soil standard sample),GBW07985(soil standard sample),GBW07406a(soil standard samp le),GBW07103(rock standard sample), GBW0731 1 (water system standard sample), GBW07312 (w ater system standard sample). National Ore Standa rd:GBW07240, GBW07241.

For the Ag, Mo, Pb standard sample series S0~S8, national-level synthetic silicate spectrometry analytical standard substance GSES I-1~GSES I-9 were selected.For Sn(283.99nm), synthetic silicate spectrometry analytical standard substances GSES I-1~GSES I-10 were used as its standard sample series S0~S9, for Sn(242.17nm),synthetic silicate spectral analysis standard materials GSES I-5~GSES I-11 were used as its standard sample series S6~S10. the national levelore standard material GBW07241 and the substrate according to the mass ratio of 1:1 mixed to formulate the standard material series point S11, the national level ore standard material GBW07241 as a standard series point S12, each sample and buffer according to the mass ratio of 1:1 mix, grind fully After covering the crucible mouth with cling film in the vibration stirrer vibration 10min to be used, the content of each element in the standard series is shown in Table 1.

Table 1 Contents of elements in the standard series

element	Standard series($\mu g \cdot g^{-1}$)												
	S0	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12
Sn(283.99nm)	0.28	0.58	1.1	2.1	5.1	10	20	50	100	200			
Sn(242.17nm)					5.1	10	20	50	100	200	500	850	1700
Ag	0.034	0.064	0.11	0.21	0.51	1.0	2.0	5.0	10.0				

Mo	0.21	0.51	1.0	2.0	5.0	10	20	50	100				
Pb(283.306nm)		2.5	5.5	10.5	20.5	50	100	200	500				
Pb(266.316nm)			5.5	10.5	20.5	50	100	200	500	1000			

2.3. Analytical Steps

Accurately weigh the dried particle size less than 74μm0.0500g sample, 0.0500g substrate and 0.1000g spectral buffer in 5mL porcelain crucible, poured into the agate mortar and fully ground for 2min, and then transferred to the original ceramic crucible, add a small clean agate beads and cover the crucible lid, placed in a vibration stirrer stirring mixing, rotational speed 2500r/min.After mixing, compact the two lower electrodes, flatten their surfaces, put 2 drops of 2% sucrose ethanol solution on them, and dry them in a 70℃ constant temperature drying box for 1h.and then use CCD-I AC arc direct reading atomic emission spectrometer to carry out two overlapping registrations of the vertical pair of electrodes under the condition of humidity lower than 40% and room temperature (22±2)℃.The spectra were taken at a room temperature of (22±2)℃ and a humidity below 40%.

3. Results and Discussion

3.1. Selection of Sample, Substrate, and Buffer Ratios

Buffers play an important role in emission spectrometry analysis by diluting the sample, preventing sample splashing, stabilizing the arc, controlling the arc temperature, and regulating the evaporation behavior of the element under test, thus being able to improve the accuracy and reliability of the analytical results[6]. For high-content tin geochemical samples, simply adding too much buffer can improve the upper limit of Sn determination, but the lack of similar matrix components leads to poor precision of the analytical results and increase the detection limit of other elements. To address this problem, an appropriate amount of matrix can be added to reduce the differences in the composition and properties of the samples under test, which is conducive to reducing the influence of components and lowering the background [12]. Therefore, it is crucial to choose the appropriate mixing ratio of sample,matrix,and buffer. In this study, the national standard substances GBW07312, GBW07406a, and GBW07240 were selected as the samples to be tested according to the ratios of samples, matrices, and buffers of 2:1:1,1:2:1,and 1:1:2, and the resulting mean, accuracy, and precision were calculated, and are shown in Table 2, in which the measured values were In the table, the measured value is the average value of 12 measurements of the same sample, the accuracy is the logarithmic deviation(ΔlogC) between the measured value and the recognized value,and the precisionis the RSD of the relative standard deviation.The experimental results show that when the ratio of the sample, substrate, and buffer is 1:1:2,the accuracy and precision of each element are best, and all of them are in line with the specification requirements.

Table 2 Experimental results of different proportions of sample,substrate and buffer

Internal standard element	Element	Certified value **(μg/g)**	**2:1:1**			**1:2:1**			**1:1:2**		
			Measured value(μg/g)	ΔlogC	RSD (%)	Measured value (μg/g)	ΔlogC	RSD (%)	Measured value (μg/g)	ΔlogC	RSD (%)
GBW07312	Sn	54	56.9	0.023	9.88	52.0	0.016	8.16	55.2	0.01	6.59
	Ag	1.15	1.18	0.012	8.68	1.13	0.009	6.66	1.16	0.005	5.56
	Mo	8.4	8.73	0.017	9.11	8.09	0.017	7.40	8.66	0.013	5.62
	Pb	285	293	0.013	8.87	280	0.008	8.23	281	0.006	6.73
GBW07	Sn	439	454	0.015	8.97	420	0.019	7.49	430	0.01	6.38
	Ag	0.24	0.248	0.014	8.55	0.236	0.007	8.04	0.245	0.009	5.45

406a	Mo	169	-	-	-	-	-	-	-	-	-
	Pb	478	491	0.012	7.70	486	0.007	6.33	472	0.005	6.19
GBW07240	Sn	1400	1467	0.02	9.57	1454	0.016	8.73	1431	0.01	6.53
	Ag	8.3	8.53	0.012	8.94	8.49	0.01	6.08	8.13	0.009	5.82
	Mo	4.2	4.30	0.01	9.08	4.40	0.02	8.78	4.33	0.013	6.21
	Pb	0.26	-	-	-	-	-	-	-	-	-

Note: "-" indicates that the content is too low or too high, exceeding the lower or upper limit of the method.

3.2. Selection of Grinding and Mixing Conditions

In plane grating arc direct reading emission spectrometry, the particle size and mixing homogeneity of the mixture(sample,substrate, spectral buffer) have a decisive influence on the precision and accuracy of the analytical results, especially for the high tin content samples, the consistency of the particle size of the mixture as well as the mixing homogeneity are directly related to the reliability of the results of the determination of the high tin content. On the basis of previous research [2-3,14], three national standard substances GBW07103, GBW07406, GBW07311 were selected to test whether the mixture was ground and vibration-mixed after drying, and the first group of tests was to grind for 2 min without vibration mixing, and the second group of tests was to vibration mix directly for 10 min without grinding, and the third group of tests was to grind for 2 min without vibration mixing. The third group of tests was carried out after grinding for 2min and then vibration mixing for 10min, the accuracy and precision of each test is shown in Table 3.The experimental results show that the mixture after grinding for 2min and then vibration mixing for 10min can effectively improve the accuracy and precision of the analytical results.

Table 3 Influence of Grinding and mixing on the determination results of Sn,Ag,Mo and Pb in CRMs

Element	Item	The first group			The second group			The third group		
		GBW07103	GBW07406	GBW07311	GBW07103	GBW07406	GBW07311	GBW07103	GBW07406	GBW07311
Sn	Certified value(μg/g)	12.5	72	370	12.5	72	370	12.5	72	370
	Measured value(μg/g)	13.1	75	384	12.9	70.7	381	12.2	73	358
	ΔlogC	0.019	0.015	0.016	0.013	0.008	0.013	0.010	0.006	0.014
	RSD(%)	9.87	8.57	9.55	9.58	8.92	7.93	7.64	6.57	7.01
Ag	Certified value(μg/g)	0.033	0.2	3.2	0.033	0.2	3.2	0.033	0.2	3.2
	Measured value(μg/g)	0.034	0.208	3.06	0.034	0.204	3.29	0.032	0.205	3.14
	ΔlogC	0.011	0.017	0.02	0.007	0.009	0.011	0.008	0.011	0.008
	RSD(%)	8.91	8.11	7.39	9.27	9.17	6.81	8.27	7.91	5.96
Mo	Certified value(μg/g)	3.5	18	5.9	3.5	18	5.9	3.5	18	5.9
	Measured value(μg/g)	3.62	18.5	6.17	3.37	17.2	5.69	3.53	18.5	6.02

	ΔlogC	0.014	0.012	0.02	0.016	0.019	0.016	0.004	0.012	0.009
	RSD(%)	7.96	9.01	8.23	8.21	9.18	6.60	6.82	8.01	6.34
Pb	Certified value(μg/g)	31	314	636	31	314	636	31	314	636
	Measured value(μg/g)	32.5	325	665	30	303	653	32	311	617
	ΔlogC	0.020	0.015	0.019	0.018	0.016	0.012	0.015	0.005	0.013
	RSD(%)	9.33	7.25	9.77	9.12	7.19	8.10	7.89	6.43	6.04

3.3. Selection of Internal Standard Elements and Analytical Line Pairs

In the quantitative analysis of solid state emission spectrometry(SSES), the introduction of a suitable internal standard element is important to eliminate or reduce the effects caused by the interference of the complex matrix of the sample, the fluctuation of the experimental conditions, and the instability of the light source, thus improving the accuracy and precision of the analytical method. Based on the principles of internal standard element selection, the element Ge was used as the internal standard element in this study and added to the buffer in the form of GeO_2[4,15]. The results shown in Fig.1 indicate that under the selected experimental conditions, the evaporation behavior of the internal standard element Ge is basically consistent with that of the element to be analyzed.

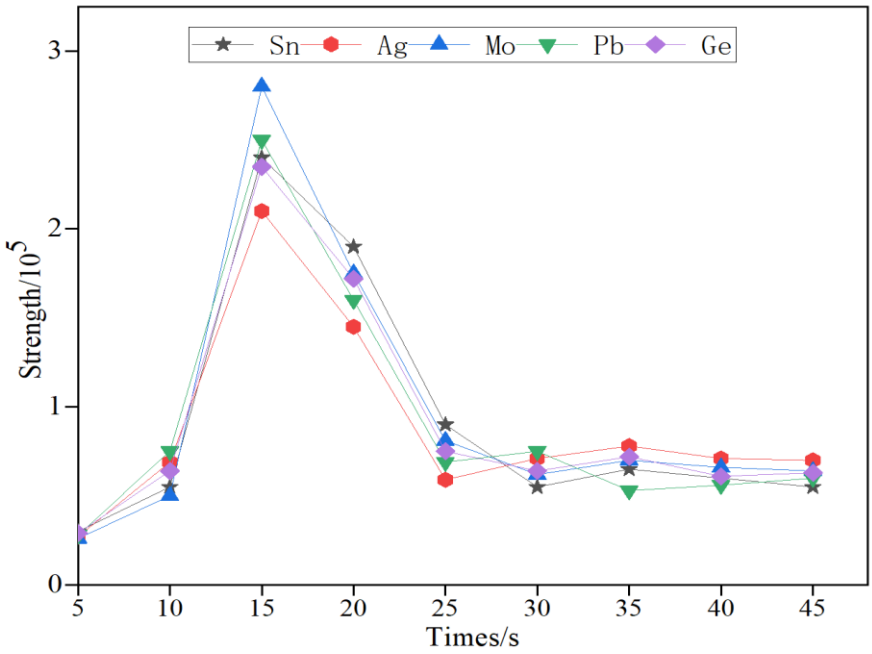

Figure 1 Evaporation curve of each element

Due to the complex matrix properties of geochemical samples, when a single spectral line is used for the measurement of high-content tin samples,selfabsorption of the spectral line or bending of the standard curve often occurs, which seriously affects the accuracy of the analytical results[6]. In order to accurately obtain the full content of tin in the sample and the analysis results of silver, lead, molybdenum and other elements, in the experimental process, should be selected as far as possible, there is no mutual interference between each other, and at the same time, similar chemical properties and response characteristics of the same similar wavelength analytical lines and internal standard lines, so as to form a pair of analytical lines[13]. The analytical lines of the internal standard Ge

element are short-wave (270.96nm) and long-wave (326.95nm) spectral lines. Based on this, the analytical line pairs listed in Table 4 were selected for measurement in this study, which can be measured directly without dilution of high content Sn samples,and the results obtained can meet there levant test requirements.

3.4. Detection Limit of the Method

The synthetic silicate spectrometry standard material matrix GSESI, which is close to the blank, was selected as the blank sample and mixed with the buffer at the mass ratio of 1:1. Under the selected experimental conditions, it was determined 12 times consecutively, and the detection limit of the method was set at three times the standard deviation of the analytical results. The res ults are shown in Table 4.

Table 4 Analyticalline pairs, determination ranges and detection limits of elements

Element	analytical line (nm)	internal standard line (nm)	measurement range(μg/g)	detection limit of the method(μg/g)
Sn	283.99	270.96	0.129~200	0.129
Sn	242.17	270.96	100~1700	15.59
Ag	328.07	326.95	0.01~10	0.01
Mo	317.03	326.95	0.085~100	0.085
Pb	283.31	270.96	0.875~200	0.875
Pb	266.32	270.96	100~1000	18.62

3.5. Precision and Accuracy of Methods

Four national-level standards containing Sn different content segments of aquatic sediments GBW07302, soil standards GBW07572 and GBW07980, rock standard GBW07727, were selected, and 12 parallel determinations were carried out respectively under the above experimental conditions to calculate the precision and accuracy of the method, and the results are shown in Fig. 2 and Fig. 3.The relative standard deviation of the determination results(RSD) is bet ween 4.98% and 8.96%, which fully meets the requirement that RSD should be less than 10% in the specification of DZ/T0011-2015. the average value of the determination of each element is basically consistent with the recognized value, and the accuracy of (|ΔlogC|) is not greater than 0.1, which is in line with the requirement that the |ΔlogC| value in the specification of DZ/T0011-2015 is not higher than 0.1, indicating that the method results are stable and accurate.

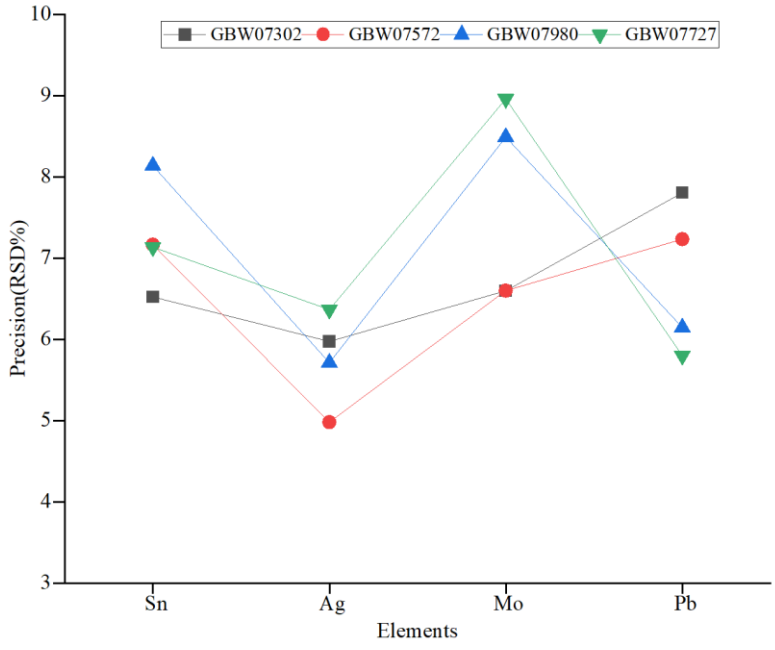

Figure 2 Precision tests of the method

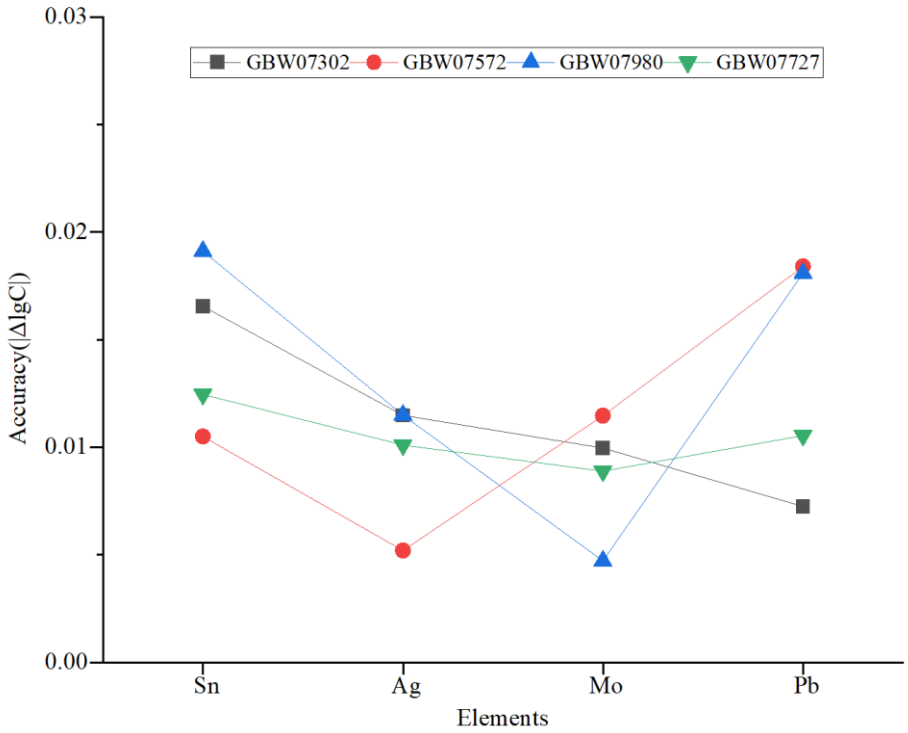

Figure 3 Accuracy tests of the method

3.6. Sample Analysis

Eight geochemical samples with high tin content in the project were taken. Sn and Pb were determined by ICP-AES, and Mo and Ag were determined by ICP-MS. and compared with the results of the analytical step 1.3 of this method, and the results are shown in Table 5.

Table 5 Determination results of Sn,Ag,Mo,Pb in samples μg/g

Element	Sample 1		Sample 2		Sample 3		Sample 4	
	Proposed method	Other method	Proposed method	Other method	Proposed method	Other method	Proposed method	Other method
Sn	17.8	19.2	35.4	37.7	107	99.3	249	262
Ag	0.20	0.18	0.37	0.35	2.07	2.31	1.25	1.12
Mo	3.56	3.39	2.74	2.93	4.69	4.37	10.1	10.5
Pb	156	164	393	379	70.8	69.2	42.5	44.0

Element	Sample 5		Sample 6		Sample 7		Sample 7	
	Proposed method	Other method	Proposed method	Other method	Proposed method	Other method	Proposed method	Other method
Sn	486	467	679	705	998	1052	1557	1483
Ag	0.082	0.088	0.11	0.12	0.15	0.14	0.43	0.39
Mo	6.54	6.75	8.38	8.12	4.07	4.22	5.41	5.20
Pb	82.7	80.3	266	251	33.4	34.6	107	103

The data in Table 5 show that the CCD-I type plana grating electric arc direct reading emission spectrometry is consistent with the results of other methods.

4. Conclusion

In this study, a method for the simultaneous determination of tin, silver, molybdenum and lead in high-tin geochemical samples by CCD-I plana grating electric arc direct reading emission spectrometer was established. This method is easy to operate without sample dilution, broadens the range of tin determination, and has less

environmental pollution, which is in line with the concept of green chemistry. The detection limits of Sn-Ag-Mo-Pb were 0.129μg/g, 0.01μg/g, 0.085μg/g, 0.875μg/g, which were better than those of the geochemical census, and the results were verified by the national standard substances and compared with other methods.It is suitable for the analysis and testing of high content tin geochemical samples.

Author contribution statement

Daolu Bu: Performed the experiments; analysis tools or data;Wrote the paper.

Shunxiang Wang:Conceived and designed the experiments,Wrote the paper.

Yang Ding: Performed the experiments.

Lihua Wang: Analyzed and interpreted the data.

Xin Xia: Conceived and designed the experiments.

Wang Rui: Performed the experiments.

Linyang Shuai: Contributed reagents, materials, Wrote the paper.

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Data Availability Statement

Data will be made available on request.

Declaration of Competing Interest

The authors confirm that there is no conflict of interest involve with any parties in this research.

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