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Synthesis and Application of a New Functionalized Resin in On-Line Preconcentration of Lead

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Abstract: An on-line system for preconcentration and determination of lead at $\mu g\ L^{-1}$ level is proposed. Amberlite XAD-2 functionalized with 2-(2′-benzothiazolylazo)-p-cresol (BTAC-XAD) packed in a minicolumn was used as sorbent. Chemical and hydrodynamic variables were evaluated and the results demonstrated that lead can be determined using sample pH at 7.0–7.5, elution with $0.050\ mol\ L^{-1}$ HCl and a sample flow rate of $6.0\ mL\ min^{-1}$. Enrichment factors of 19, 43, and 60 were achieved by using the time-based technique with preconcentration periods of 60, 120, and 180 s, respectively. Detection limit (3s) was $1.7\ \mu g\ L^{-1}$ when used preconcentration time of 180 s. This procedure was applied to lead determination in natural water samples. Accuracy of procedure was confirmed by lead determination in certified reference materials.

Keywords: BTAC, functionalization, lead, FAAS, amberlite XAD-2

INTRODUCTION

Lead is a toxic metal that occurs naturally in the earth's crust, in ores such as lead sulphide PbS (galena). However, as a result of human activity, in the atmosphere nowadays lead is found mainly as $PbSO_4$ and $PbCO_3$. This metal can be absorbed through ingestion into the gut (e.g., drinking of lead-containing water), through inhalation—occupationally or environmentally of either

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inorganic or organic forms, or through the skin (1). Determination of lead in natural waters, biological matrices, sediments, etc., is a very important topic, considering that the concentration of this metal can serve as base to characterize the level of pollution of a certain area.

Lead concentrations in natural waters are very low. So, very sensitive analytical techniques of detection are required as Electrothermal Atomic Absorption Spectrometry (ETAAS) or Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) and Flame Atomic Absorption Spectrometry (FAAS) has not sufficient sensitivity for some determinations, so these techniques require the use of a preconcentration step in order to reach an appropriate detection (2, 3).

On-line systems in which solid-phase extraction (SPE) is involved always take place in two steps that involve sorption and elution. Many procedures of preconcentration can be found in literature employing a variety of materials, such as chelating (4) or polymeric (5–7) resins, ion-exchangers (8, 9), functionalized silica (10–12), activated alumina (13, 14), polyurethane foam (15), carbon (16), or fullerene (17). Lead determinations have been performed in on-line systems using solid-phase extraction with some materials cited previously and spectrometric detection (18–20).

The development of chelating sorbents for use in metal preconcentration systems has been a subject of increasing interest. To produce these matrices, chelating ligands can be loaded on solid supports (20–23) or can be covalently bonded to a polymeric matrix through an azo (24–27) or methylene group (28–31).

Azo reagents have been used in spectrophotometric determinations due to their capacity to form complexes with a large variety of metals (32). Sorption or functionalization of these reagents in polymeric matrices is a good alternative for enrichment procedures (33, 34).

In this work, an on-line preconcentration method has been developed for determination of lead using a minicolumn packed with Amberlite XAD-2 support functionalized with 2-(2′-benzothiazolylazo)-p-cresol (BTAC) reagent. BTAC have been used in spectrophotometric determinations (35, 36) and preconcentration procedures (37). The synthesis of the chelating resin was followed by the study of chemical and hydrodynamic parameters. The developed method has been applied to the trace determination of lead in natural waters and biological material.

EXPERIMENTAL

Instrumentation

A Varian Model SpectrAA 220 (Mulgrave, Victoria, Australia) flame atomic absorption spectrometer equipped with a deuterium arc was used for the analysis. The lead hollow cathode lamp was run under the conditions suggested by the manufacturer (current: 7.5 mA). Also the wavelength (283.3 nm), the bandwidth of the slit (0.5 nm), and burner height (13.5 mm) had conventional values. The flame composition was acetylene (flow rate 2.0 l min^{-1}) and air (flow rate 13.5 l min^{-1}). Nebulizer flow rate was 5.0 mL min^{-1}. Infrared spectra were recorded in an ABB Bomen MB series model MB100 Fourier transform IR spectrometer. A Thermo Finnigan Flash elemental analyzer 1112 series was used for elemental analysis.

The diagram of the on-line preconcentration system for lead preconcentration is shown in Fig. 1. The manifold was adapted to the nebulizer system of the flame atomic absorption spectrometer. The flow system was made up of a peristaltic pump (Alitea C-6 XV, Stockholm, Sweden) furnished with Tygon tubes to deliver all solutions, two Rheodyne 5041 (Cotati, CA) six-port valves to select elution and preconcentration steps, and a BTAC-XAD packed minicolumn for the online preconcentration of lead. The manifold was built up with PTFE tubing of 0.5 mm bore. To minimize dispersion, the length of the PTFE capillary tube between the end of minicolumn and the nebulizer was as short as possible (about 5 cm). A Digimed DM 20 (Santo Amaro, Brazil) pH meter was used for pH monitoring.

The laboratory-made cylindrical minicolumn with 3.50 cm length and internal diameter of 4.0 mm contains about 100 mg of BTAC-XAD. A syringe was used to put the sorbent in column. Plastic foams were placed at both sides of minicolumn to keep the packing material in place. Afterward, the column was washed with ethanol, 5% (v/v) nitric acid solution and deionized water,

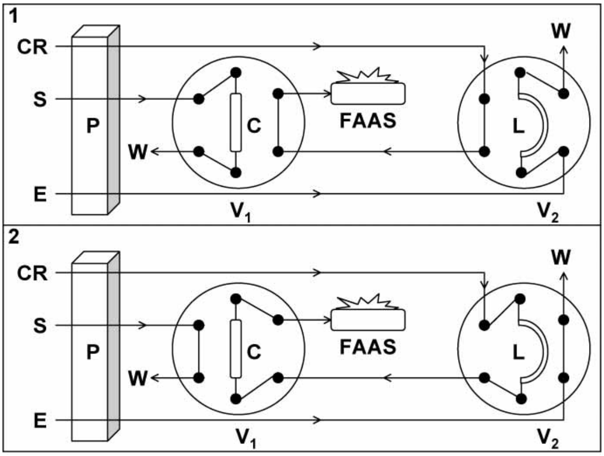

Figure 1. Schematic diagram of the flow system used to preconcentration and determination of lead by FAAS. S: sample; E: eluent; CR: carrier; P: peristaltic pump; C: BTAC-XAD minicolumn; V_1 and V_2: six-port valves; L: loop; FAAS: flame atomic absorption spectrometer and W: waste. 1 = system in the preconcentration step and 2 = system in the elution position.

respectively, at 2.50 mL min^{-1} flow rate. Washing with nitric acid and ethanol was necessary in order to prevent any metal or organic contamination, respectively.

Reagents

Ultrapure water from an Easypure RF water purification system (Barnstead, Dubuque, USA) was used to prepare all solutions. All reagents were of analytical reagent grade. Lead(II) working solutions at μg L^{-1} level were prepared daily by diluting a 1000 μg mL^{-1} lead solution (Merck). Hydrochloric acid solutions to elution were prepared by direct dilution with deionized water from the concentrated suprapur solution (Merck). The laboratory glassware was kept overnight in a 5% v/v nitric acid solution. Afterward, it was rinsed thoroughly with ultrapure water. Acetate, tris(tris-(hydroxymethyl)aminomethane), borate and ammoniacal buffers conveniently prepared (38) were used to adjust the sample pH in the range 4.8–6.0, 7.0–10.0, 8.0–9.0, and 9.0–10.0, respectively. Amberlite XAD-2 (Sigma, 20–60 mesh), nitric and sulfuric acids (Merck), and sodium hydroxide and nitrite (Reagen) were used for synthesis of the sorbent. The reagent 2-(2-benzothiazolylazo)-p-cresol was produced in laboratory as described previously (30).

Synthesis of the Resin

Procedure described in the literature for similar materials was used to synthesis of BTAC-XAD (26, 27). Amberlite XAD-2 (5 g) was treated with 10 mL of concentrated HNO_3 and 25 mL of concentrated H_2SO_4 and the mixture stirred at 60°C for 1 h on a water bath. Thereafter, the reaction mixture was poured into an ice–water mixture. The nitrated resin was filtered, washed repeatedly with water until free from acid, and thereafter treated with a reducing mixture of tin(II) chloride, concentrated hydrochloric acid, and ethanol. The system was refluxed for 12 h at 90°C. The precipitate was filtered off and washed with water and 2 mol L^{-1} NaOH. The amino resin was first washed with 2 mol L^{-1} HCl and finally with ultrapure water to remove the excess of HCl. It was suspended in an ice–water mixture (150 mL) of 1 mol L^{-1} HCl and 1 mol L^{-1} $NaNO_2$. The diazotized resin was filtered, washed with ice-cold water, and reacted with BTAC (0.5 g in 250 mL of 5% (w/v) NaOH solution) at 0–5°C for 24 h. The resulting dark-purple resin was filtered, washed with water, and dried in air.

Sample Preparation

For accuracy studies, two certified reference materials (CRMs) furnished by National Institute of Standards and Technology (Gaithersburg, MD), NIST 1572 Citrus Leaves and International Atomic Energy Agency (Vienna, Austria) MA-B-3/TM Fish Tissue were analyzed. For their decomposition

(27), about 0.4 g of material was treated with 4.0 ml of 1 : 1 (v/v) nitric acid solution and kept overnight in Teflon vessel. Afterward the Teflon vessel was closed and put into a pressurized digestion system. The thermal heating was carried out in a stove at 150°C for 12 h. After cooling at room temperature these solutions were adjusted to pH with a 10% (w/v) sodium hydroxide solution and appropriate buffer solution. After the volume was made up to 50 mL and diluted conveniently.

Natural waters were sampled in one well, one river, four lagoons, and two beaches at Salvador, BA, Brazil. For these samples, the only pretreatment was acidification to pH 2.0 with nitric acid, which was performed immediately after collection, in order to prevent adsorption of the lead (II) ions on the flask walls. After the samples were filtered and 30 mL of the filtrate were taken the pH was adjusted by addition of 5 mL of buffer solution. The volume was then made up to 50 mL. At least one blank solution was run for each sample in order to evaluate lead contamination by the reagents used.

On-Line Preconcentration System

The flow system was operated in a time-based mode. A sample solution (S) containing lead was kept at convenient pH with a buffer solution and was percolated through a minicolumn that retained the cation. Then, lead(II) ions were retained onto the minicolumn and the remaining solution was discharged (W). Carrier (CR) was taken directly to the nebulizer of the flame atomic absorption spectrometer while the eluent was filling the loop (L) and flowing to waste (W). Turning two valves simultaneously, the carrier transports the eluent through the column, displacing lead ions. This eluate is taken to the spectrometer. Signals were measured as peak height by using FAAS software. It was read four times and averaged. It was not necessary to recondition the minicolumn at the end of each cycle since samples were buffered before preconcentration.

RESULTS AND DISCUSSION

Resin Characterization

Elemental analysis (found: C, 65.5%; H, 3.8%; N, 17.9%; calculated for $C_{22}H_{17}N_5OS$: C, 66.2%; H, 4.3%; N, 17.5%) have shown that on an average one BTAC molecule is present in the resin per repeat unit of the polymer. A structure according with elemental analysis is shown in Fig. 2. Infrared spectrum of BTAC-XAD resin was compared with that of free Amberlite XAD-2. There are additional bands at 3520-3400, 1540, 1455, and 1340 cm^{-1}, which appear to originate due to modification of resin by the

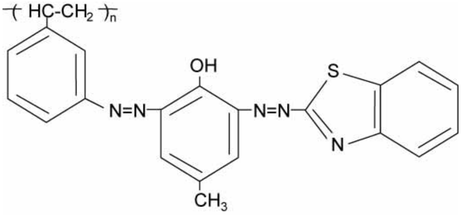

Figure 2. Proposed structure for BTAC-XAD.

ligand and are characteristic of O–H, –N═N–, C–N, and C–OH vibrations, respectively.

Chemical Variables

A lead solution containing 100.0 μg L^{-1} was employed for chemical variables studies. Lifetime of column packed with BTAC reagent immobilized on Amberlite XAD-2 resin was monitored. It was made measuring the signal of a 100.0 μg L^{-1} lead solution at the end of each day of work and counting the number of cycles. Results demonstrated that column showned good performance for at least 500 cycles.

The effect of the sample pH on the lead response was investigated within the range of 3.5–10.0. Results of this study are shown in Fig. 3. Maximum retention occurred within the pH range of 7.0–9.2 using borate buffer. Then, pH range of 7.0–7.5 was selected for subsequent work, because the use of lower pH values results in more selective determinations.

Elution of lead from the sorbent material was studied with acidic solutions because the sorption of the metal in column occurs under neutral to basic conditions. For this experiment, hydrochloric acid solutions at different concentrations (0.005 to 2.00 mol L^{-1}) were used as a stripping agent. Total elution was reached in concentrations over 0.025 mol L^{-1}, according to Fig. 4. So, 0.050 mol L^{-1} hydrochloric acid was selected as eluent for further studies. The influence of the volume of the eluent loop (L) was also studied, because it indicates the quantity of acid that passes by column. It was found that for an eluent loop larger than 35 μL the signal is constant. So, a volume of 40 μL of L was chosen for posterior experiments.

Hydrodynamic Variables

A 100.0 μg L^{-1} lead solution was also employed to study hydrodynamic variables. Sample flow rate is an important parameter because it determinates the contact time between sorbent and analyte. The effect of sample flow rate was studied by varying flow rates from 1.0 to 12.0 mL min^{-1}. As the amount

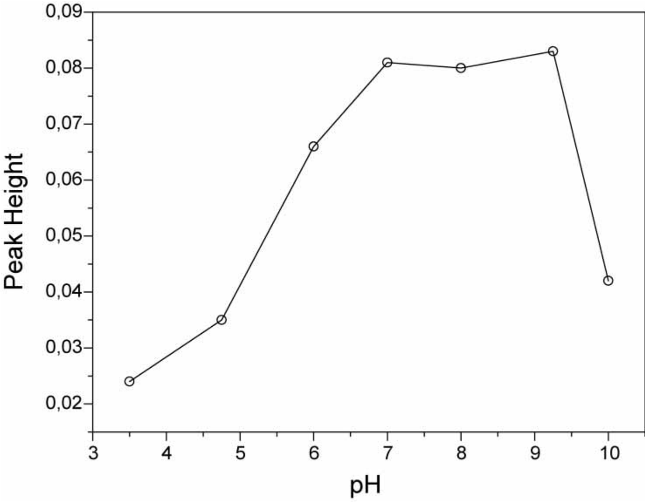

Figure 3. Effect of pH on the preconcentration of lead.

of sample varies with flow rate if preconcentration time is constant, for this experiment, a volume of 5.00 mL of a lead solution was pumped in order to maintain the sample amount invariable. Analytical signals decreased slightly at flow rates upper 5.5 mL min^{-1}, as shown in Fig. 5. These results indicate that lead sorption is minor at high flow rates because lead(II) ions pass by column too quickly so that the time between the phases is not sufficient for a significant retention. Moreover, high flow rates increase back-pressure and

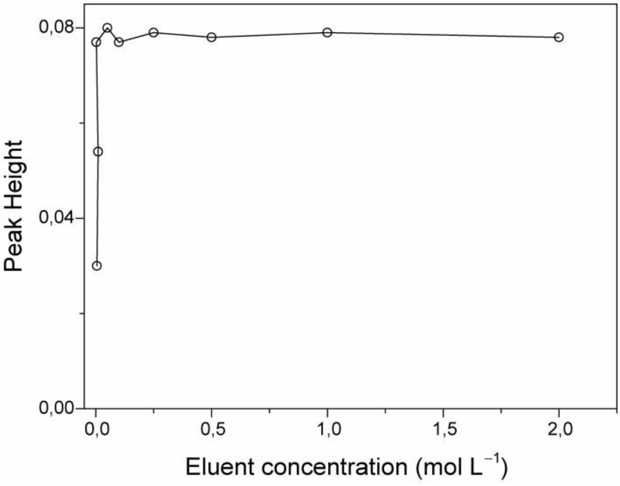

Figure 4. Effect of eluent concentration on the preconcentration of lead.

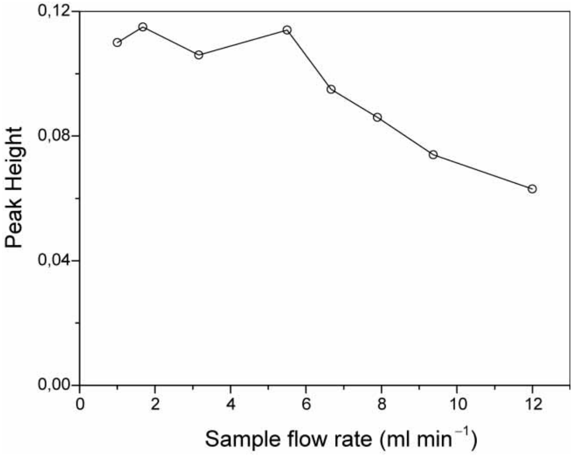

Figure 5. Effect of sample flow rate on the preconcentration of lead.

this could cause leakage. Thus, a flow rate of 5.0 mL min^{-1} was chosen for posterior experiments as a compromise between efficiency and stability of system.

The effect of the carrier flow rate in the step of lead desorption from the sorbent was also investigated because it establishes the velocity of the eluent through minicolumn. Results showed that the analytical signal is maximum and constant at flow rates within the range of 4.0 to 7.5 mL min^{-1}. At flow rates less than 4.0 mL min^{-1} the analytical signal considerably decreased, resulting in broader peaks. Probably, it is due to incompatibility between elution and nebulization flow rates, which cause significant dispersion when eluent flow rate is smaller than nebulizer flow rate. So, in posterior experiments an eluent flow rate of 5.0 mL min^{-1} was used to combine elution and aspiration.

Transfer phase factor was also determined for the solid phase BTAC-XAD. It is a parameter defined as the ratio between analyte mass in original sample solution and in the concentrate after elution (9). For this experiment, a volume of 10.0 mL of a 500.0 μg L^{-1} lead solution was percolated by the column. So, the elution was performed, and a volume of 1.00 mL of the concentrate containing the analyte was collected. Lead amount in this solution was directly determined by FAAS. Working with sample flow rate of 5.00 mL min^{-1}, transfer phase factor obtained for the system was 0.85.

Preconcentration time in the on-line system was studied in the range from 0.5 to 4.0 min. The FAAS analytical signal increased proportionally with the preconcentration time up to 3.0 min, which means that transfer phase factor is constant within this time interval. A preconcentration time of 2.00 min was chosen to combine sensitivity and efficiency. However, when more sensitive determinations are required, as lead determination in natural waters, preconcentration time was increased to 3.0 min.

Effect of Foreign Ions

Solutions containing lead (100.0 μg L^{-1}) and other ions in order to determine the selectivity of analytical systems were prepared and the developed procedure was applied. The effect of each species was considered interference when the signal in the presence of the species resulted in a deviation of the signal by 5%. The following ions in the concentrations are in the brackets: Na^{+1} (17 g L^{-1}), K^{+} (1.5 g L^{-1}), Ca^{+2} (400 mg L^{-1}), Al^{+3}, Ba^{+2} and Mg^{+2} (100 mg L^{-1}), Fe^{+3} and Zn^{+2} (2.5 mg L^{-1}), Cd^{+2} and Cu^{+2} (500 μg L^{-1}), Ni^{+2} and Co^{+2} (100 μg L^{-1}), PO_4^{-3} (150 mg L^{-1}), NO_3^{-} and SO_4^{-2} (1.5 g L^{-1}), and Cl^{-} (17 g L^{-1}) do not interfere in the determination of lead.

Analytical Features

The solid-phase flow system allowed the preconcentration of lead under the optimum chemical and flow conditions. Characteristic data are given in Table 1. The data are shown for 60, 120, and 180 s preconcentration time. By using direct aspiration in FAAS without the preconcentration system, linear range for lead determination was between 49.0 and 5000.0 μg L^{-1} and linear equation was $A = 0{,}00416 + 2{,}92 \times 10^{-5}C$, where A is the absorbance and C is the metal concentration in solution (μg L^{-1}). Enrichment factors were calculated as the ratio of the slopes of the calibration graphs with preconcentration and direct aspiration, respectively (9, 39). Other factors that characterize on-line preconcentation systems, such as concentration efficiency (CE) and consumptive index (CI) (9), were also determined.

Table 1. Analytical characteristics of the on-line lead preconcentration system using BTAC-XAD minicolumn

Preconcentration time, s	60	120	180
Enrichment factor	19	43	60
Concentration efficiency, min^{-1}	16	19	18
Consumptive index, mL	0.26	0.23	0.25
Sample frequency, h^{-1}	51	27	18
Limit of detection, μg L^{-1}	6.5	4.3	1.7
Precision, %	6.5–4.7	5.7–1.2	5.8–3.6
Linear range, μg L^{-1}	6.5–600.0	4.3–500.0	1.7–300.0
Calibration function	$A = 9.83 \times 10^{-3} + 5.70 \times 10^{-4\circ}C$	$A = 1.28 \times 10^{-2} + 1.25 \times 10^{-3}C$	$A = 1.00 \times 10^{-2} + 1.76 \times 10^{-3}C$

Accuracy of the Method

In order to evaluate the accuracy of developed procedure, the following certified reference materials were analyzed: NIST 1572 Citrus Leaves and IAEA (MA-B-3/TM) Fish Tissue. The results are described in Table 2. Confidence intervals are at 95% level. It was found that there is no significant difference between achieved results by proposed method and certified results.

Application

The analytical system was used for lead determination in natural water samples. The results are described in Table 3. Recoveries (R) of spike additions (10.0, 25.0, or 50.0 $\mu g\,g^{-1}$) to water samples were quantitative (93–107%). R was calculated as follows: $R\ (\%) = \{(C_m - C_o)/m\} \times 100$, where C_m is a value of lead in a bland sample (a spike sample), C_o is a value of lead in a sample, and m is the amount of lead spike. These results proved also that the procedure is not affected by high concentrations of alcaline and alcaline earth metals.

CONCLUSION

The proposed method can be used routinely in the laboratory for lead quantification in waters and biological material. The reagent BTAC functionalized in Amberlite XAD-2 support, resulted in a chelating system used successfully in on-line preconcentration of lead. The on-line preconcentration system significantly improved FAAS performance, resulting in a simple and sensitive analytical procedure. Selectivity of FAAS allows lead determinations in the presence of significant amounts of foreign substances generally present in natural waters. The system also shows simplicity, because it involves only two steps, elution and preconcentration. It is very attractive in laboratories

Table 2. Lead determination in certified reference materials (n = 4)

	Lead amount ($\mu g\ g^{-1}$)	
Sample	Proposed methodology	Certified
Citrus leaves NIST 1572	12.9 ± 2.2	13.3 ± 2.4
Fish tissue IAEA MA-B-3/TM	4.2 ± 0.5	4.4 ± 0.6

IAEA—International Atomic Energy Agency.
NIST—National Institute of Standards & Technology.

Table 3. Results obtained for lead determination in water samples (n = 4)

Sample	Added ($\mu g\,L^{-1}$)	Lead found by methodology proposed[a] ($\mu g\,L^{-1}$)	Recovery (%)
Lagoon water 1	0.0	<LOD	—
	25.0	24.1 ± 0.6	96
	50.0	49.6 ± 2.1	99
Lagoon water 2	0.0	<LOD	—
	25.0	25.2 ± 1.0	101
	50.0	51.9 ± 3.4	104
Lagoon water 3	0.0	8.3 ± 1.1	—
	25.0	31.6 ± 0.8	93
	50.0	57.8 ± 2.4	99
Lagoon water 4	0.0	11.7 ± 1.4	—
	10.0	22.3 ± 2.1	106
	25.0	37.9 ± 3.6	105
River water	0.0	9.5 ± 0.9	—
	10.0	18.9 ± 1.1	94
	25.0	35.2 ± 2.5	103
Well water	0.0	<LOD	—
	25.0	26.8 ± 2.2	107
	50.0	52.7 ± 2.3	105
Seawater 1	0.0	<LOD	—
	25.0	25.7 ± 0.6	103
	50.0	50.9 ± 2.1	102
Seawater 2	0.0	<LOD	—
	25.0	25.5 ± 0.4	102
	50.0	50.3 ± 1.1	100

[a] Confidence interval 95%, LOD: Detection limit.

for routine analysis, equipped with only FAAS equipment for metal determination.

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