DETERMINATION OF EUROPIUM BY AAS WITH ELECTROTHERMAL ATOMIZATION

Josef KOMÁREK and Mojmír GÁNÓCZY

Department of Analytical Chemistry, Masaryk University, 611 37 Brno

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A WETA all-tungsten atomizer and a tungsten probe in conjuction with a graphite atomizer were used for the electrothermal atomization of europium. The life of the tungsten probe was extended by combining it with a pyrolytically coated graphite tube fitted with tantalum lining and using argon–hydrogen atmosphere. The sensitivity of europium determination in the tungsten atomizer was increased by adding La^{3+} in a concentration of 0·02 g l^{-1}.

In the lanthanoid series, europium (and also ytterbium) has a special position. Many of its characteristics depart from the linear dependences on the atomic number, which can be ascribed to a pronounced tendency of this element to occur in oxidation state II. As compared to other lanthanoids, europium has a markedly lower density, lower melting and boiling points, lower heats of sublimation and vaporization, and a different crystal structure[1]. As a consequence, this element is easier to atomize than the remaining rare earth elements.

In solution, this analyte is predominantly present in the Eu^{3+} form. After water evaporation, the temperature increase is accompanied by conversion of the salts to the oxide. Eu_2O_3 is stable up to 1 000°C; at higher temperatures it degrades to EuO (refs[1,2]), whose dissociation energy is 479 kJ mol^{-1} (ref.[3]). Carbide, if formed, is not very stable, the europium vapour pressure in contact with EuC_2 reaching 1 Pa at a temperature as low as 1 130°C (ref.[4]). In tungsten atomizers, atomization of rare earth elements proceeds via thermal dissociation of the monoxides in the solid phase.

For the majority of lanthanoids, atomization of the oxide proceeds faster in argon–hydrogen atmosphere than in pure argon[2]. Apparently, hydrogen in the metallic atomizer acts as a reductant. In graphite atomizers, this role can be taken over by carbon, which is present not only on the tube surface but also in the gas phase[5]. Carbon also penetrates into the tube space through tantalum lining if this is employed to coat the graphite; it diffuses through the tantalum foil in the tantalum carbide form from the side of direct contact with the graphite wall.

The complex atomic spectra of lanthanoids, comprising a large number of lines, cause considerable spectral interferences. Still, for europium, measured at 459·4 nm, interferences have only been reported to arise from Fe, Ca and Al, which absorb at this wavelength[6]. Chemical interferences, affecting immediately the atomization process, are more frequent. Haines[3] tested the effect of La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Y in a hundredfold excess over the analyte, and did not observe more than 10% increase or decrease in the absorbance pulse. A substantial signal drop for 1 ng of Eu was found in the presence of 1, 10 and 100 μg of La and Yb (ref.[7]).

The present work deals with the potential of the tungsten atomizer and of the tungsten probe in the determination of europium; the effect of salts is also investigated.

EXPERIMENTAL

Solutions and Apparatus

Standard solution of Eu^{3+} was prepared by dissolving 115·8 mg of dry Eu_2O_3 of spectral purity (Spolana, Neratovice) in 8·3 ml of concentrated HCl of reagent grade purity, and diluting to 100 ml with redistilled water. The solution was standardized via chelometric titration with EDTA in urotropine medium using xylenol orange as the indicator; it contained Eu^{3+} in a concentration of 0·998 $g\,l^{-1}$.

Solutions of $ScCl_3$, YCl_3, $Ce(NO_3)_4.2\,NH_4NO_3$, $LaCl_3$, $CaCl_2$, $SrCl_2$, $BaCl_2$, $Ba(NO_3)_2$, $MgCl_2$, $AlCl_3$, $Al(NO_3)_3$ were prepared in metal concentrations of 1 or 10 $g\,l^{-1}$ from salts of reagent grade purity. Solutions of Nd^{3+}, Ho^{3+}, Tb^{3+} and Yb^{3+} were prepared by dissolving Nd_2O_3 99%, Ho_2O_3 pure, Tb_4O_7 of spectral purity (all Lachema, Brno) and Yb_2O_3 "Specpure" (Johnson Matthey, London), respectively, in HNO_3 1 : 1 and diluting with water to the concentrations as above.

Measurements were performed on a Perkin–Elmer 3030 atomic absorption spectrometer. The 459·4 nm radiation source was an Intensitron hollow-cathode lamp; current was 35 mA, transmitted spectral interval 0·2 nm. A WETA-80 tungsten atomizer (Prague Institute of Chemical Technology and Brown Coal Research Institute in Most) was used for atomization; it was equipped with a head adapted for all tungsten tube profiles (15 mm length) in the WETA-82 instrument. A Perkin–Elmer HGA-74 graphite atomizer with the tube coated with pyrolytic graphite was used for atomization from the tungsten probe. Sample dispensing onto the probe was made manually using a 5 μl Eppendorf pipette; dispensing of 10 μl volumes on the WETA atomizer wall or 20 μl volumes on the HGA-400 atomizer wall was provided by an AS-1 autosampler. The whole instrument set was synchronized and controlled by the control module of the HGA-400 atomizer.

The pyrolytic graphite layer in the graphite tube was prepared by in situ pyrolysis[8]. Tantalum cover was obtained by lining the pyrolytically coated graphite tube with a tantalum foil. For this reason, a 15 × 18 mm rectangle was cut from a foil 0·15 mm thick, and a 2 × 5 mm oval hole for the probe was cut in it 3 mm from the upper side. The foil was rolled up to the form of tube 15 mm long and 5 mm in diameter and inserted into the graphite tube so that the holes in the tube and in the foil coincided. On a slow heating to 2 600°C the foil adhered to the graphite tube, and the atomizer was ready for measurement.

The tungsten probe was made from a tungsten sheet 0·15 mm thick; this was obtained from the edges of worn profiles for the WETA-82 atomizer (Fig. 1). The edges were cut off with scissors to a 15 × 4·5 mm strip, which was adjusted to a width of 4 mm by grinding on a fine disk sander. For the two sides, narrows were then ground into the strip so that a neck 1·2 mm was formed. This separated the 4 × 4 mm area for a sample from the remaining part by which the strip was clamped in a cylindrical holder. The holder with the probe was inserted into a device for the probe moving in and out by means of two electromagnets[9]. A maximum of 5 μl of sample could be injected onto the probe. The sample dispensing and drying proceeded off the graphite tube. Heat for sample drying was provided by the hot tube. Thereafter the probe was slid into the tube and decomposition took place. The probe was allowed to rest inside the tube during the cooling of both, the probe and the tube. Then it was taken out, the tube was heated to the atomization temperature, and the probe was inserted into the tube. The spectrometer recording was activated immediately before inserting the probe. After the tube cooling the probe was taken out again and made ready for further sample dispensing.

In this work, the amount of europium corresponding with the absorbance of 0 0044 was regarded as characteristic. The limit of determination corresponds with the amount (or the concentration) related to the absorbance $A = \bar{A}_{bl} + 10s_{bl}$ where $\bar{A}_{bl}$ is the average absorbance of the blank and s_{bl} is the standard deviation of the blank for 6 measurements. The precision of the measurement was determined as the relative standard deviation of the analytical signal for five independent measurements.

Determination of Europium in Bastnesite Concentrate

The sample (0·8 g) was carried into 30 ml of HCl (1 : 1), several drops of 30% H_2O_2 were added, and the mixture was heated to boil. After complete decomposition, the solution was evaporated to dryness, and 5 ml of HCl (1 : 1) and 2 drops of 30% H_2O_2 were added. The system was allowed to stand for 10 min, diluted with 30 ml of hot water, and allowed to stand for another 12 h. Thereafter the system was filtered, the residue was rinsed with hot water, and the filtrate was diluted with water to 100 ml (Filtrate 1). The filter with the residue was ignited in a platinum crucible and the combustion residue was heated with a mixture of 10 ml of HF and 2 ml of $HClO_4$. The evaporation residue was ignited at 950°C and melted with approximately 3 g of a sodium carbonate–borax 3 : 1 mixture. The melt was leached with water, the leachate allowed to stand, the formed precipitate filtered off and the filtrate diluted with water to 200 ml (Filtrate 2). The precipitate on the filter was dissolved in a mixture of HCl (1 : 1) and H_2O_2, which was added dropwise, and the solution was diluted with water to 50 ml (Filtrate 3). Finally, the filtrates were diluted with 0·01M-HCl up to a 150-fold excess and its 10 μl injected into the WETA atomizer (Table I). The standard additions method was used for evaluation.

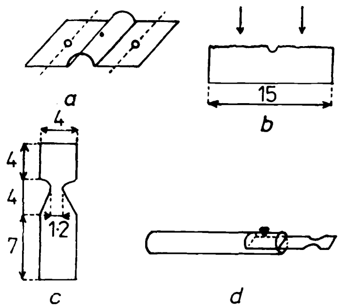

FIG. 1

Tungsten probe (size in mm): *a* cutting edges from WETA profiles, *b* grinding, *c* shape of the probe, *d* clamping of the probe

Determination of Europium in Aluminate-Type Luminophors

The sample (0·2 g) was melted with 1 g of Na_2CO_3 and 1·5 g of borax in a platinum crucible. After cooling, the melt was dissolved in 20 ml of 4M-HCl and the solution diluted to 50 ml with water. This solution was successively diluted 1 000 and 10 times by 0·01M-HCl and $LaCl_3$ was added (resulting La^{3+} concentration was 0·02 g l^{-1}). 10 μl of this solution was injected into the tungsten atomizer and atomized under conditions given in Table I. After each determination the empty tube was fired at 3 000°C for cleaning. The calibration curve resulted from standards in 0·01M-HCl in the presence of La^{3+} ions (resulting concentration 0·02 g l^{-1}).

RESULTS AND DISCUSSION

Atomization of Europium from the Tungsten Atomizer

The absorbance signal of europium was constant up to the decomposition temperature, 1 800°C, at which the atomization signal of europium began to appear. As the heating rate was raised up to 9 K ms^{-1}, the absorbance pulse increased; at higher heating rates it was constant. The peak area did not change. The europium signal increased with increasing amount of hydrogen added to argon (2·5 l min^{-1}). First the peak height rise was very rapid, but slowed down at a hydrogen flow rate of 0·5 l min^{-1}. The increase was very small at higher hydrogen flow rates. The peak area increased with the hydrogen flow rate increasing up to 0·5 l min^{-1}, and decreased slightly at flow rates in excess of 0·75 l min^{-1}. The optimum atomization conditions are given in Table I, the calibration curve parameters are given in Table II. The effect of acids is shown in Fig. 2. Hydrochloric acid exerted no effect and can be recommended for sample treatment. A concentration of HCl of 0·01 mol l^{-1} was used for the analysis.

The effect of salts of Mg^{2+}, Al^{3+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, the silicate matrix, Sc^{3+}, Y^{3+}, La^{3+} and some lanthanoids was examined (Figs 3, 4). The interfering effect of salts of Ca^{2+}, Sr^{2+}, Ba^{2+}, La^{3+} and lanthanoids is different from that of Al^{3+}, Mg^{2+} and SiO_3^{2-}. Strontium in μg-amounts or more exhibited an interfering effect due to its emission, which dropped the signal under the baseline at the beginning of the absorbance pulse. Since the time of the emission by strontium was shorter than that of the europium absorbance pulse, the end of the latter still appeared in the time record. Seeking for the cause of the interference, the emission profile of strontium was measured under the same conditions as applied to the atomization of europium. The band maximum was found at 460·8 nm, a wavelength corresponding exactly to that of the atomic line of strontium. The half band width, however, was approximately 0·9 nm and the radiation intensity at 459·4 nm (europium line) still reached 5% of the maximum value. This atomic line broadening can be partly explained by the high temperature and increased pressure during the fast temperature rise in the tube.

During the europium determination in real samples such as bastnesite concentrate, where it occurs in low concentrations and Ca and other elements are present, the standard additions method can be applied to eliminate the effect.

TABLE I

Optimum conditions for the atomization of europium in the WETA tungsten atomizer and in the HGA-400 graphite atomizer with the pyrolytically coated tube

Particular step	WETA[a]		HGA	
	t, °C	τ, s	t, °C	τ, s
Drying	95	30	—	—
	160	15	150	35
Decomposition	500	5	—	—
	1 500, 1 200[b]	15	1 200	20
Atomization	2 700[c]	2·5	2 600[d,e]	5
Firing for cleaning	3 000[f]	1	—	—

[a] Argon and hydrogen flow rates 2·5 l min^{-1} and 0·6 l min^{-1}, respectively; [b] for practical samples; [c] t_R = 10 K ms^{-1}; [d] t_R = 0 (t_R is temperature increase rate); [e] argon flow stopped; [f] after addition of $LaCl_3$.

TABLE II

Charaoteristics of calibration plots for the determination of europium by electrothermal atomization in a WETA tungsten atomizer (A), in the same atomizer applying matrix modification with La^{3+} ions (0·02 g l^{-1}) (B), on the tungsten probe in a pyrolytically coated tube (C) and in the tube lined with tantalum (D), and using a graphite tube with pyrolytic coating (HGA) (E)

Characteristics	A	B	C	D	E
Volume dispensed, μl	10	10	5	5	20
Upper limit of linearity, pg	430	190	800	390	1 200
Characteristic amount P_{Ch}, pg	4·0	1·9	7·0	3·6	14·5
Limit of determination L_Q, pg	41	19	89	45	133
Concentration limit of determination $L_{Q,c}$, μg l^{-1}	4·1	1·9	18	9·0	6·7

Negligible amounts of europium were present in Filtrate 2. The relative standard deviation for the total 0·06% Eu was lower than 5%. The calibration curve method is inappropriate in this case, the sensitivity of determination being affected by the composition of the matrix. Figure 5 shows the atomization curves of the europium standard in the absence and presence of $CaCl_2$. The temperature at which signal appears remains unchanged, but atomization in the presence of $CaCl_2$ is higher

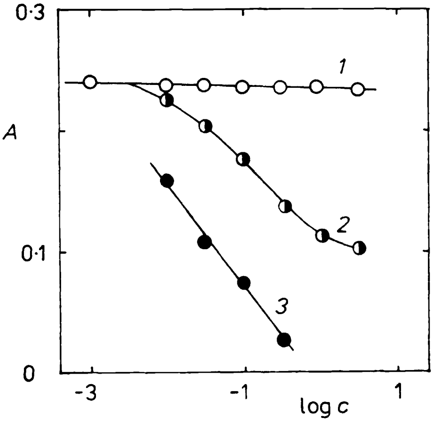

FIG. 2

Effect of acids (c in mol l^{-1}) on the absorbance of europium (0·2 ng) during the atomization in a tungsten atomizer. Acid: *1* HCl, *2* HNO_3, *3* H_2SO_4

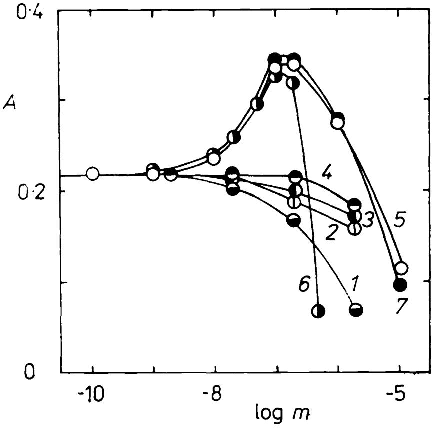

FIG. 3

Effect of alkaline earth, aluminium and silicate (m in g) on the atomization of europium (0·2 ng) in the tungsten atomizer. Salt: *1* $AlCl_3$, *2* $Al(NO_3)_3$, *3* $MgCl_2$, *4* K_2SiO_3, *5* $CaCl_2$, *6* $SrCl_2$, *7* $BaCl_2$

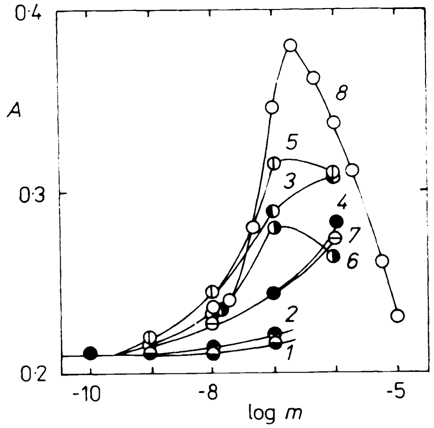

FIG. 4

Effect of scandium, yttrium, lanthanum and other lanthanoids (m in g) on the atomization of europium (0·2 ng) in the tungsten atomizer. Cation: *1* Sc^{3+}, *2* Y^{3+}, *3* Ce^{4+}, *4* Yb^{3+}, *5* Nd^{3+}, *6* Tb^{3+}, *7* Ho^{3+}, *8* La^{3+}

at higher temperatures. Figure 6 shows the shape of the absorbance pulse. Most of the examined elements affected the absorbance pulse as Ca or Ba did, i.e., caused its narrowing and increase; only with Sc and Y this effect was not observed. In the presence of salts of Ca^{2+}, Sr^{2+}, Ba^{2+}, La^{3+} and other lanthanoids, the rate of the atomization reaction is probably affected. For Ce, Yb and Ho, the europium signal drop with increasing interferent concentration was not observed. The highest signal increase occurred in the presence of $LaCl_3$ at a La^{3+} concentration of $20\,mg\,l^{-1}$ (i.e., amount of 200 ng). The characteristics of the calibration curve for europium in the presence of La^{3+} at this concentration are given in Table II. The use of calibration curve method in the presence of $LaCl_3$ can be recommended for samples containing europium in amounts higher than 1‰; for the dilution used, the matrix element concentrations are then negligible with respect to the concentration of present lanthanum and they do not affect the signal height. In the analysis of dilute luminophor solutions in 0.01M-HCl using the standard additions method, the calibration dependences for different samples had different slopes, and the relative standard deviations for luminophor samples containing 2·5–3‰ Eu were 2–14‰. Applying the calibration curve method with the addition of $LaCl_3$, the relative standard deviations for the same samples were 2–6‰. The results agreed well with those obtained by emission spectrometry in the nitrous oxide–acetylene flame[10].

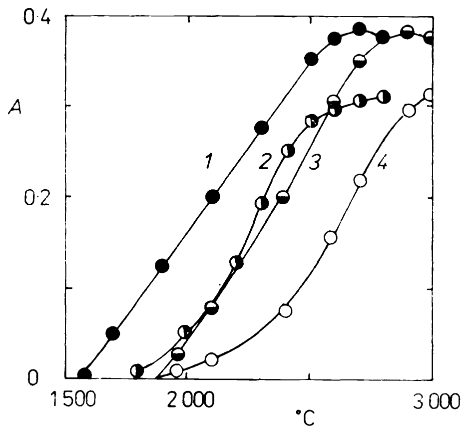

Fig. 5

Atomization plots for europium using the pyrolytically coated graphite tube (*1*, *2*) or tungsten atomizer (*3*, *4*). Amounts used: *1* 1 ng of Eu with 200 ng of La, *2* 1 ng of Eu, *3* 0·2 ng of Eu with 100 ng of Ca, *4* 0·2 ng of Eu

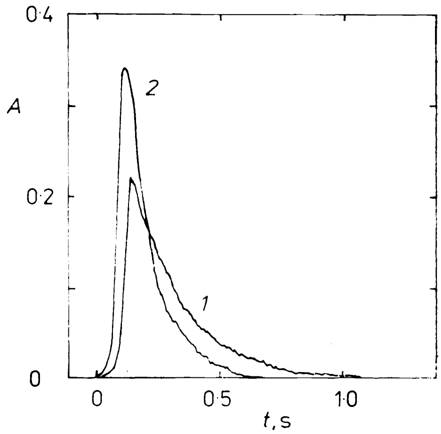

Fig. 6

Effect of Ca^{2+} or Ba^{2+} on the absorbance signal of europium from the tungsten atomizer. Amounts used: *1* 0·2 ng of Eu, *2* 0·2 ng of Eu with 100 ng of Ca^{2+} or Ba^{2+}

Atomization from the Tungsten Probe

Atomization from the tungsten probe began to appear at 1 800°C in the pyrolytically coated tube and at 2 100°C in the tube lined with tantalum. The highest signal was at 2 600°C. While testing the life of the probe inserted into the tube with pyrolytic graphite, the europium signal in conditions given in Table III was found constant for the first ten determinations, the relative standard deviation was 0·6 – 3%. Afterwards the signal decreased and the relative standard deviation increased to 6 – 7%. The probes became brittle in several atomization cycles due to the formation of tungsten carbide and to the rapid temperature changes. In approximately 30 cycles the probes began to change in shape due to inner strain, they deformed in a screw-like form, and in approximately 40 cycles they broke about the edge of the tube. In the case of the tantalum-lined tube in argon the signal was about 4 times lower under the same conditions; an argon–hydrogen mixture with optimum flow rates of 50 and 20 ml min^{-1}, respectively, was therefore used in the atomization. At the beginning the absorbance signal was only slightly higher than in the case of the pyrolytically coated unlined tube. In 15 ignitions, however, the signal increased, the relative standard deviation decreased and became steady at 6 – 8%. The probe life exceeded 50 atomization cycles. In this arrangement the limiting factor is the tantalum lining rather than the probe itself. Slight disturbance of the foil does not pose problems since the solution does not come in direct contact with it. The calibration curve characteristics are given in Table II.

No effect of La^{3+} on the absorbance signal of europium was observed when working with a pyrolytically coated tube; in the tantalum-lined tube, on the other

TABLE III

Conditions for the atomization of europium from the tungsten probe

Particular step	Tube temperature °C	Time s
Drying	1 200	40
Decomposition	1 200	20
Cooling	20	15
Heating	2 600	10
Atomization[a]	2 600	6
Firing for cleaning	2 600	3
Cooling	20	15

[a] For the pyrolytically coated tube, argon flow stopped; for the tube lined with tantalum foil, argon and hydrogen flow rates 50 and 20 ml min^{-1}, respectively.

hand, the dependence was similar to that found in the tungsten atomizer (Fig. 7). For the tungsten probe inserted into the tantalum foil-lined tube the characteristic amount is lower than in the case of the tungsten atomizer, whereas if the atomization takes place from the probe inserted into the pyrolytically coated tube this amount is twice higher. Atomization from a probe exhibits some advantages over that from the tantalum-lined tube wall. Tantalum lining does not permit high heating rates to be applied. During the atomization from a probe the tube heating can be slow without affecting negatively the sensitivity of determination, although sensitivity changes during the probe life have to be checked periodically by measurements on standard solutions.

Atomization from the Wall of the Pyrolytically Coated Graphite Tube

The optimum conditions and sensitivity of determination of europium applying atomization from the wall of the pyrolytically coated graphite tube are given in Tables I and II.

The effect of $LaCl_3$ was similar to that for the tungsten atomizer, although the maximum was attained at lanthanum amounts about one order of magnitude higher (Fig. 7), but in such case the amount of europium introduced into the graphite tube was 5 times higher in comparison with that introduced into the tungsten atomizer. In he presence of $LaCl_3$ the atomization curve was shifted to lower temperatures when compared to that in the absence of this salt (Fig. 5). During the atomization of samples containing lanthanum, the tube properties changed, a lanthanum memory effect appeared. The surface layer affected the determination and lanthanum-free solutions gave signals similar to those in the presence of lanthanum. Table II demonttrates that the sensitivity is lowest in the pyrolytically coated graphite tube; on the

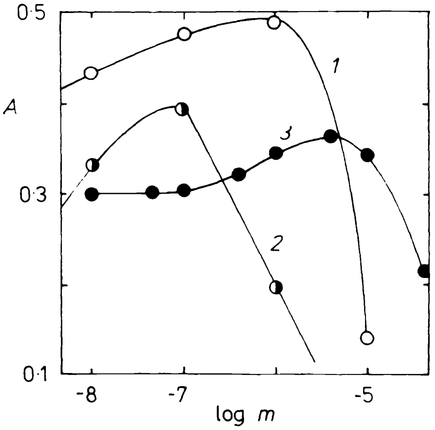

Fig. 7

Effect of $LaCl_3$ (m of La^{3+} in g) on the absorbance signal of europium. Conditions: *1* 0·4 ng of Eu, tungsten probe and tube with tantalum lining, hydrogen flow rate 20 ml min^{-1}; *2* 0·4 ng of Eu, tungsten probe and tube with tantalum lining, hydrogen flow stopped during atomization; *3* 1 ng of Eu, tube coated with pyrographite, argon flow stopped during atomization other hand, larger solution volumes can be injected into this atomizer than into the tungsten atomizer or onto the probe. Thus, with respect to the concentration limit of determination, the atomization in the pyrolytic tube is superior to the atomization from the probe.

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