Quantitative Speciation of Mn-Bearing Particulates Emitted from Autos Burning (Methylcyclopentadienyl)manganese Tricarbonyl-Added Gasolines Using XANES Spectroscopy

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The chemical nature of Mn-containing particulates emitted from (methylcyclopentadienyl)manganese tricarbonyl-added gasoline engines has been elucidated using Mn K-edge X-ray absorption fine structure (XAFS) spectroscopy. Edge shift data from the X-ray absorption near-edge structure (XANES) spectra showed that the average Mn valence in these particulates is ~2.2. Using a principal component analysis (PCA) algorithm, the number and type of probable species contained in these particulates were determined to be three, consisting of Mn3O4, Mn5SO4·H2O, and a divalent manganese phosphate, Mn3(PO4)2(PO3·H2O)·4H2O. The proportions of these Mn phases in each particulate sample were evaluated quantitatively using least-squares fitting (LSF) of the experimental XANES spectra with linear combinations of these principal component (model compound) spectra. Two groups of Mn-bearing particulates may be distinguished: group I having 4–9 wt % of Mn3O4 and exhibiting a single intense first major absorption maximum at the Mn K-edge and group II containing 15–22 wt % of Mn3O4 and exhibiting a doublet absorption maximum at lower intensity. Fourier transforms of the EXAFS signals were found to corroborate the XANES results. This study clearly establishes XANES spectroscopy, in combination with PCA and LSF, as a quantitative analytical tool for speciation of dilute and/or amorphous multicomponent environmental materials not easily attainable with conventional methods.

Introduction

The potential health effects of airborne particulate matter (PM) have recently prompted considerable debate. This debate centers upon the efficacy of new PM standards proposed by the U.S. Environmental Protection Agency (EPA) given the high cost estimated to achieve the new PM standard (1). To date, there is little information about the chemical nature of PM or the health effects associated with PM in outdoor or indoor air. Upon recommendation of the National Academy of Sciences and congressional mandate, the EPA has expanded its efforts to obtain detailed knowledge about particulate matter with the goal of implementing control measures for PM on a more solid and sound scientific basis.

One important research topic concerns the identification of chemical species in PM and the methods used to evaluate particulate chemical composition. This information could prove very important when addressing source apportionment issues and evaluating the effect of PM on air quality. The present work was undertaken to develop a spectroscopic tool to speciate compounds that exist in dilute and/or amorphous phases within airborne particulates. The subject of the work is Mn-bearing materials emitted from vehicles operating on fuels containing a manganese-based fuel additive.

(Methylcyclopentadienyl)manganese tricarbonyl (MMT) is a fuel additive for enhancing fuel efficiency and decreasing emission in automobiles. Environmental concerns about airborne Mn-bearing particulates and their potential health effects require intensive studies regarding the form and distribution of manganese emitted from the automotive engine (2). The effect of using MMT-containing gasoline on vehicle emissions along roadways (3) and ambient manganese levels (4) have been the subject of extensive study. In the period 1990–1994, a series of assessments of the potential health risks associated with the use of an MMT additive in unleaded gasoline was performed by the EPA (5–6). These led to the identification of a key health issue associated with inhalation exposure to Mn-bearing particulates resulting from the combustion of MMT in gasoline. A number of research areas have also been proposed to address potential manganese exposures associated with use of MMT, toxicological end points, as well as certain pharmacokinetic and emission characterization issues (7). Moreover, it is well-known that certain species of manganese are highly soluble and other species are not. Thus, depending on the species of manganese inhaled, more or less manganese may be absorbed into the blood. In addition, it has been suggested that differences in the valence state of inhaled manganese may result in differences in distribution or toxicity (6). It is important, therefore, to determine the composition of actual Mn-bearing particulates emitted by vehicles burning fuels containing MMT. The chemical knowledge is a prerequisite to pharmacokinetic studies for appropriate choice of atmosphere and other issues pertaining to the design of animal testing, such as proper dosage to provide insight into which species of manganese are most problematic in terms of delivery to the brain.

X-ray diffraction measurements (8) yielded little or no information due to a combination of insufficient sample mass, amorphous nature of the particulate matter, and/or small particle size. Studies of four relatively heavily loaded samples (292–4244 μg) showed only background from the filter substrate material. ESCA measurements identified O, P, and S as major elements likely to be associated with the Mn-bearing exhaust particulates. Mn, P, and S 2p and O 1s core-level spectroscopy indicated that the vehicle exhaust may contain manganese primarily in the form of a manganese phosphate and/or sulfate (8). Thus, the physicochemical nature of these Mn-bearing exhaust particulates is largely unknown and not well-characterized.

XAFS (X-ray absorption fine structure) spectroscopy (9) using intense synchrotron radiation appears to be the method
of choice for chemical speciation of PM and other environmental materials that are generally low in concentration and/or small total sample size. This technique is atomic specific and sensitive to low concentration (10 ppm or lower) as well as low sample mass (less than μg with third generation synchrotron sources). Sample crystallinity is not required since XAFS is a structural probe sensitive to short-range order. Chemical information such as valence, coordination geometry, bond distance, and ligand coordination number can be obtained with high accuracy in combination with use of appropriate model compounds and theoretical FEFF simulations (10, 11).

Furthermore, this tool can now be rendered quantitative in multicomponent systems of environmental concern (12–16) and with uniqueness as is demonstrated in this work.

We have, therefore, applied Mn K-edge XAFS spectroscopy to characterize exhaust particulates sampled in a controlled manner from a pair of sister vehicles running MMT-containing gasoline and various EPA standardized test cycles. Using a set of preselected manganese model compounds, the Mn-bearing components in the exhaust particulates were speculated by first utilizing a PCA algorithm to determine the minimum number and type of probable components and then quantified from the experimental XANES spectra using a least-squares fitting (LSF) procedure. Analysis of the EXAFS spectra at higher energies using the standard Fourier transform procedure has been used to substantiate findings from the XANES data.

### Experimental Section

#### Particulate Samples

The Mn-bearing particulate samples were collected at Southwest Research Institute in San Antonio, TX. Teflon-coated fiber glass filters 47 mm in diameter were used. Two identical 1997 Ford Taurus vehicles (3.0-L V6), denoted as vehicles A and B, were employed to generate the particulates under four test cycles. Samples were collected after 4000 and 40 000 mi of operation on gasoline containing Mn2P2O7 was synthesized by heating MnPO4 at 700 °C for 19 h. The phase purity of these model compounds was examined using in-house X-ray powder diffraction, which showed no detectable impurity Bragg lines in each material used.

#### XAFS Measurements

XAFS measurements were performed on beamline 10-2 (18) at Stanford Synchrotron Radiation Laboratory (SSRL) with SPEAR (Stanford Positron Electron Accumulation Ring) operating at an electron energy of 3.0 GeV and injection current at ~100 mA. The synchrotron beam from the wiggler was apertured with a 0.5-mm vertical entrance slit and monochromatized using a Si(220) double crystal, which was 50% detuned to minimize higher harmonics. For bulk model compounds, a conventional transmission mode was used to collect the absorption spectra. For the particulate specimens with low Mn concentration, a fluorescence detection mode utilizing a Lytle detector was used (19). The monochromatic beam incident on the sample had a footprint 2 mm high × 28 mm wide for maximum sample coverage. All spectra were collected in the QEXAFS mode (20). Multiple scans varying from 4 sweeps for XANES and 8 sweeps for EXAFS were performed to ~1000 eV (~16 Å−1) above the Mn K-edge to yield optimal S/N ratios. An equivalent step size of 0.25 eV/point was used for XANES scans, and one of 1.0 eV/point was used for EXAFS scans. A run as described above. After the completion of the second stabilized phase, the vehicle was subjected to a 600-s engine-off soak. After the soak, the transient and stabilized phase was repeated 13 additional times. Each repeat was separated by the 600-s engine-off soak. The total run time for each FTP test was 343 min or 5 h and 43 min. A more severe California Unified Driving Cycle (UDC) as recommended by the EPA was also used. This driving cycle contains higher speeds and accelerations than found in the FTP cycles. After a cold start, bags 1 and 2 of the UDC were repeated 14 times. Each repetition was separated by a 600-s soak followed by a hot starts. Over the UDC cycle, the vehicle operated an equivalent of 137-mi travel. The FTP inactive catalyst test cycle was similar to the normal FTP except that the inactive catalyst was placed on the vehicle.

#### Model Compounds

These include a series of manganese oxides and oxohydroxides: MnO, MnO2, Mn2O3, β-MnO2, and α-MnO(OH); selected divalent salts: MnS, MnSO4·H2O, Mn2P2O7, and MnPO4; and Mn(PO4)(PO3(OH))2·4H2O (hureaulite, abbreviation MnPhos used in this paper); and trivalent MnPO4. The choice of these model compounds was guided by ESCA identification (8) of O, P, and S associated with the exhaust particulates as well as thermodynamic considerations at the fuel combustion conditions (17). The oxides, sulfate, MnPhos, and MnPO4 were procured from Alfa Aesar; MnS was from Aldrich; and manganese metal powder was from Cerac. MnPO4·H2O was synthesized by heating MnPO4 at 700 °C for 19 h. The phase purity of these model compounds was examined using in-house X-ray powder diffraction, which showed no detectable impurity Bragg lines in each material used.

### Table 1: History of Mn-Bearing Particulates: Vehicle, Mileage Accumulation, and Test Cycle Used

<table>
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<th>E0 positiona (eV)</th>
<th>valence</th>
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a. The observed XANES spectral features tabulated here are discussed in the text. b. E0 is measured with respect to the Mn metal K-edge at 6539 eV. c. From normalized XANES spectra.
manganese metal standard foil located in front of a reference ion chamber was measured simultaneously with each spectral sample for in-situ energy calibration.

Data Analysis

**Energy Calibration and Normalization.** Data reduction of experimental XAFS spectra was carried out using the software WinXAS97 v.2.1 (21). The energy threshold $E_{\text{ref}}$ of the reference metal foil was determined from the first inflection point in the spectrum (22), and raw data were linearly calibrated against the difference between the obtained $E_{\text{ref}}$ and the tabulated absorption edge energy for Mn K edge at 6.539 keV (23). Pre-edge background subtraction and XANES normalization were carried out by fitting a linear polynomial to the pre-edge region and a cubic polynomial to the postedge region of the absorption spectrum. A smooth atomic normalization was carried out by fitting a linear polynomial to each of the four XANES spectra of synthetic mechanical mixtures with varying amounts of MnO and Mn$_3$O$_4$. The target transformation consists of a multiplication of a column matrix $E$ containing the eigenvectors, the transpose of this matrix, and the vector $T$ as shown in eq 3. If $T$ and $T^*$ are identical within experimental errors, the vector $T$ is indeed included in the vector subspace and is a principal component of the input vector set given in the column vectors of matrix $A$.

Finally, to utilize target transformation, an XANES spectrum of a pure reference compound after interpolation onto the same energy grid as the unknown spectra may be multiplied with the eigenvector column matrix according to eq 3. A good agreement (direct superimposition, with a residual < 1.0%, for example) of the reference spectrum and the experimental XANES spectra calculated by SVD and target transformation have been carried out for four XANES spectra of synthetic mechanical mixtures with varying amounts of MnO and Mn$_3$O$_4$. The target...
transformation result for MnO in this ideal case is indeed indistinguishable from the experimental spectrum as expected.

**LSF of XANES Spectra.** On the basis of the obtained PCA results in terms of number and probable type of constituent (reference) species in the exhaust particulates, a LSF procedure was then applied to determine the amount of each reference in the particulate sample. Therefore, a sum of the reference spectra was refined to each particulate XANES spectra. The employed nonlinear LSF procedure is based on the Levenberg–Marquardt algorithm (27) to minimize the difference between the experimental and the simulated XANES spectrum. A fit residual $R$ is calculated from

$$R = \sum_{i=1}^{m} \left| \mu_{i,\text{Exp}}(E) - \mu_{i,\text{Sim}}(E) \right| \times 100$$

with $\mu_{i,\text{Exp}}(E)$ as the normalized absorption of the unknown sample and $\mu_{i,\text{Sim}}(E)$ as the simulated absorption based on varying amounts of normalized reference XANES spectra.

Two free running parameters were refined for each reference spectra in the least-squares XANES fits, i.e., the partial concentration and an edge-energy correction term. The latter was included to account for minor errors in energy calibration of both the unknown spectrum and the references. A conservative estimate for errors in energy calibration is the experimental step size of the XANES spectrum. Thus, edge-energy correction terms for individual references should not be much larger than this step size. In addition, this edge-energy correction term may be used to recognize references that mathematically improve the refinement but that are not present in the unknown spectrum. In the case where the edge-energy shift exceeds many times the experimental step size, the corresponding reference is to be discarded from the fit.

**Results and Discussion**

**XAFS Spectra of Particulate Samples: Average Mn Valence.**

The normalized XANES spectra of the 12 particulated samples listed in Table 1 are shown in Figure 1. Visual examination reveals two distinct XANES patterns emerging from these exhaust particulates: group I with a single, strong absorption maximum just about the edge and group II with a doublet absorption feature at lower intensity. Samples 7–9 and 12 exhibit a group II pattern. The difference in the Fourier transforms of the extracted EXAFS signals will be shown later to correlate with the low and high Mn$_3$O$_4$ content in the transforms of the extracted EXAFS signals will be shown later. As is shown later, the intensity of this dominant XANES feature may be correlated to the concentration of Mn$_3$O$_4$ in the sample.

Two apparent trends exist. Mn content is greater for (i) UDC cycle than FTP extended as exemplified by sample 2 vs sample 1, sample 4 vs sample 3, sample 8 vs sample 7, and sample 12 vs sample 11; (ii) 40000-mi UDC than 4000-mi UDC by a factor of ~2, as exemplified by sample 4 vs sample 2 and sample 12 vs sample 8; and (iii) FTP than FTP (inactive catalyst) by a factor of ~3 as exemplified by sample 5 vs sample 6 and sample 9 vs sample 10. (i) and (ii) are to be expected since both more severe driving cycles, with lower fuel economy, longer accumulation mileage cycles, and more absolute fuel consumption, are expected to result in greater total exhaust particulates. The effect of inactive catalysts on lowering the Mn content in the exhaust particulates is not clear at the moment. Finally, the height of the first absorption maximum in the normalized XANES for the particulates is also listed in the Table 1. As is shown later, the intensity of this dominant XANES feature may be correlated to the concentration of Mn$_3$O$_4$ in the sample.

**Mn Components Speciation: PCA Results.** In this work PCA is used to determine the number and type of principal components (model compounds) that additively give rise to the set of 12 XANES spectra obtained from exhaust particu-

FIGURE 1. Experimental Mn K-edge XANES spectra of the 12 exhaust particulate samples. Indicated are sample no., vehicle, mileage, and test cycle (see also Table 1).

The experimental edge jumps for the particulate samples are also given in Table 1. The jump is a direct measure of the total Mn content in the sample. Some apparent trends exist. Mn content is greater for (i) UDC cycle than FTP extended as exemplified by sample 2 vs sample 1, sample 4 vs sample 3, sample 8 vs sample 7, and sample 12 vs sample 11; (ii) 40000-mi UDC than 4000-mi UDC by a factor of ~2, as exemplified by sample 4 vs sample 2 and sample 12 vs sample 8; and (iii) FTP than FTP (inactive catalyst) by a factor of ~3 as exemplified by sample 5 vs sample 6 and sample 9 vs sample 10. (i) and (ii) are to be expected since both more severe driving cycles, with lower fuel economy, longer accumulation mileage cycles, and more absolute fuel consumption, are expected to result in greater total exhaust particulates. The effect of inactive catalysts on lowering the Mn content in the exhaust particulates is not clear at the moment. Finally, the height of the first absorption maximum in the normalized XANES for the particulates is also listed in the Table 1. As is shown later, the intensity of this dominant XANES feature may be correlated to the concentration of Mn$_3$O$_4$ in the sample.
lates generated under different conditions. A column matrix \( A \) is constructed from the 12 XANES spectra interpolated onto the same energy grid. From the eigenvalues in the SVD output matrix \( V \), it is found that the first three eigenvectors of the \( E \) matrix are sufficient to reproduce the experimental XANES spectra with a residual of less than 1%. Hence, three principal components (i.e., manganese species) appear to be present in the exhaust particulates. In a plot of eigenvalue times weight for the first principal component versus eigenvalue times weight of the second principal component (Figure 4a), it is noted that the 12 experimental spectra are divided into two groups. These two groups are identical to the two groups described above based on the observation of whether one or two peaks in the first absorption maximum near the Mn K-edge shown in Figure 2 and shown more clearly in Figure 4b.

Target transformation was then employed to identify the probable manganese species in the exhaust particulates from the set of 10 reference compounds. These reference compounds include MnO, Mn\(_2\)O\(_3\), \( \alpha \)-MnO\(_2\), Mn\(_3\)O\(_4\), MnPO\(_4\), Mn\(_2\)O\(_2\), MnS, and MnSO\(_4\)\(_4\)H\(_2\)O. Three model compounds are found to yield a sufficient match upon transformation, namely, Mn\(_2\)O\(_3\), MnSO\(_4\)\(_4\)H\(_2\)O, and MnPhos. The corresponding XANES spectra are displayed in Figure 5a–c. On the other hand, Figure 6a,b shows the transformation results for MnO and \( \alpha \)-MnO(OH), respectively, indicating that these two manganese species are likely not present in the analyzed exhaust particulates.

Furthermore, the singlet and doublet absorption maximum feature above the Mn K-edge of groups I and II materials may be graphically realized in a composite plot with those of the identified principal components: Mn\(_2\)O\(_3\), MnSO\(_4\)\(_4\)H\(_2\)O, and MnPhos. It can be seen in Figure 4b that the higher energy feature of the doublet must arise from a substantial contribution of the Mn\(_2\)O\(_3\) component as can be shown quantitatively in the next section.

Quantification of Mn Components: Least-Squares XANES Fits. Having determined the number and type of Mn-bearing components in the 12 exhaust particulates with the PCA procedure, a nonlinear LSF procedure was then applied to quantify these components in the unknown particulate samples from their normalized experimental XANES spectra. In Figure 7, the fitted spectra (dotted lines) of a group I particulate typified by sample 1 (Table 1) and a group II particulate typified by sample 9 are superimposed with the corresponding experimental spectra (solid lines) together with the least-squares fractions of the pure model compounds making up the fitted curve. Graphically, it is obvious that the intensity of the single absorption maximum in the group I spectra is primarily a combined contribution from those of the MnSO\(_4\)\(_4\)H\(_2\)O and MnPhos components, whereas in the group II spectra additional contribution from the Mn\(_2\)O\(_3\) first absorption maximum becomes significant and gives rise to a resolvable peak at higher energy—hence the doublet feature.

Results of the least-squares fittings of the XANES data for the 12 particulate samples using linear combinations of the three major components Mn\(_2\)O\(_3\), MnSO\(_4\)\(_4\)H\(_2\)O, and MnPhos are listed in Table 2. The XANES fit percentages given in Table 2 correspond to the amount of the respective normalized reference spectra required to yield a good match between simulated and experimental XANES spectra. Uncertainties in the fit results were estimated from a variation plot of two partial concentrations shown in Figure 8a. On the average, an uncertainty limit of 5% corresponds to an error of ca. 2.0% in the fit results.

To convert XANES fit percentages into the more commonly used weight percentages, a series of synthetic binary mixtures...
of Mn₃O₄ and MnPhos was measured to generate a plot of (known) weight percent of Mn₃O₄ versus the obtained XANES fit percentage (Figure 8b). Subsequently, eq 5 was fitted to the data points and used to convert experimental XANES fit percent into weight percent of Mn₃O₄. The formalism given in eq 5 is widely used in the quantitative phase analysis of X-ray diffraction data and has been described in detail in the literature (30):

$$\mu_{i, \text{Fit}} = \frac{x_i \mu_i^o}{x_i (\mu_i^o - \mu_M^o) + \mu_M^o}$$

where $\mu_{i, \text{Fit}}$ is the Mn₃O₄ concentration determined from the

FIGURE 4. (a) Plot of PCA eigenvalues $v_i$ times weights $w_{i,j}$ of the two most important eigenvectors obtained for the 12 exhaust particulate samples. Sample numbers are those given in Table 1. Two groups can clearly be distinguished. (b) Normalized Mn K-edge XANES spectra of the three identified Mn-bearing principal components in the auto exhaust particulates and those of the groups I and II materials, indicating origin of the high energy feature of the first absorption maximum doublet in the latter group.

FIGURE 5. Target transformation results (dashed lines) for (a) Mn₃O₄, (b) MnSO₄·H₂O, and (c) MnPhos. Solid curves are the corresponding experimental XANES spectra.
least-squares fitting, $x$, the wt \% $\mu_1^*$ and $\mu_2^*$ are the mass absorption coefficients of Mn in Mn$_3$O$_4$ and in the matrix, respectively. For Mn$_3$O$_4$, a mass absorption coefficient of 344.0 cm$^2$/g and for the matrix (MnPhos in the case of the mechanical mixtures), a value of 132.0 cm$^2$/g was obtained (31).

Since a simple calibration curve such as that given in Figure 8b can only be constructed for two reference substances using eq 15, the exhaust particulate samples may be treated as pseudo-binary systems consisting of MnSO$_4$ in a homogeneous matrix of MnSO$_4$/MnPhos. Hence, only weight percent of Mn$_3$O$_4$ can be obtained together with the combined weight percent of MnSO$_4$ and MnPhos. Moreover, from consideration of stoichiometry and formula weights, in synthetic binary mixtures of MnSO$_4$ and MnPhos, it was indeed found that the XANES fitting percentages almost directly correspond to weight percentages. Thus, we conclude that the weight percent ratio of MnSO$_4$ and MnPhos can be approximated by the XANES fit percent ratio of the two compounds.

Fourier transforms of the measured EXAFS signals (shown in Figure 3) are also revealing. In Figure 9, the $k^3$-weighted Fourier transforms of the three principal components and those of groups I and II particulates are given. Fourier transforms of group II particulates exhibit a strong peak in the 3.0-Å region, which is also prominent in that for Mn$_3$O$_4$,

but not in those of the group I particulate materials. This corroborates well with the XANES simulation results summarized in Table 2.

Thus, we succeeded in speciating qualitatively and quantitatively Mn-bearing particulates emitted from automobile engines burning MMT-added gasoline using XAFS spectroscopy. The average Mn valence in the particulates is found to be $\sim$2.2. Three principal Mn-bearing components are found to present in the particulates: Mn$_3$O$_4$, MnSO$_4$·H$_2$O, and MnPhos, the concentrations of which vary depending on vehicle, driving test cycles, and mileage accumulation. The sources of S and P in the exhaust particulates are known to arise from ZDDP (zinc dialkyl dithiophosphate) additives in lubricant oil used to generate antiwear films on steel surfaces in the cylinders (32, 33). Group I particulates are high in MnSO$_4$·H$_2$O and MnPhos and low in Mn$_3$O$_4$ content (4–9 wt \%), and group II particulates are high in Mn$_3$O$_4$ (15–22 wt \%).
TABLE 2. Type and Amount of Mn-Bearing Species in Exhaust Particulates Derived from a Combination of PCA and Least-Squares Fitting of XANES Spectra

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<th>$MnSO_4$ (%)</th>
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</table>

$\sum = MnSO_4$ weight percent + MnPhos weight percent.

FIGURE 8. (a) Variation plot of partial concentration of $Mn_3O_4$ vs concentration of $MnSO_4\cdot H_2O$ obtained for sample 4. Solid curve indicates area in parameter space that corresponds to a variation in fit residual $R$ of $\sim 5\%$. Extension of ellipse on both axes was used to estimate the uncertainty, $\pm \Delta C$, in least-squares fit results. (b) Calibration curve obtained from fitting eq 5 to weight percent of $Mn_3O_4$ vs % of XANES fit for a series of binary $Mn_3O_4$–MnPhos synthetic mixtures.

FIGURE 9. $k^3$-weighted Fourier transforms of the three principal components found to contain both groups I and II particulates. It is clearly seen that the 3-Å peak in the group II materials arises from a substantial contribution from $Mn_3O_4$ (Table 2).

The work reported herein demonstrates a powerful combination of the PCA and LSF procedure for meaningful qualitative (number and type of components) and quantitative analysis of unknown mixtures from XANES data and clearly establishes XAFS spectroscopy as a quantitative analytical tool for speciation of dilute, multicomponent systems of environmental relevance.

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