APPLICATIONS OF X-RAY METHODS TO SPECIATE MANGANESE PARTICULATES FROM VEHICLES USING MMT FUEL

John G. Reynolds, and Art J. Nelson
Lawrence Livermore National Laboratory
Livermore, CA
J. Roos,
Ethyl Corporation, Richmond, VA

INTRODUCTION

Methylcyclopentadienyl manganese tricarbonyl (MMT) has been used as a fuel additive in both gasoline and diesel fuel [1]. Testing of fuels with this additive has been performed on a variety of makes and models of auto and diesel vehicles. These studies have been conducted with fuel containing MMT at a concentration of 0.03125 gram manganese per gallon. X-ray techniques (such as XAS and XPS) have been applied to samples of particulates collected from these test vehicles and engines to speciate the Mn and other metal compounds found in these exhaust particulates. Mn species such as phosphates, sulfates and oxides have been found in varying concentrations depending upon the make and model, the type of fuel, and the test conditions.

EXPERIMENTAL

Samples and techniques have been described in detail elsewhere [2]. The samples were collected using a Moudi Impactor on vehicles operated over the Urban Dynamometer Driving Schedule using a modification of the dilution tunnel technique described in 40 CFR Part 86. Seven samples were examined taken from five different vehicles: 92BR-TP (1992 Buick Regal Tailpipe), 93FE-TP (1993 Ford Escort tailpipe), 93FE-EO (1993 Ford Escort engine out), 93HC-TP (1993 Honda Civic tailpipe), 93HC-CO (1993 Honda Civic after catalytic converter), 93HC-TP (1993 Toyota Camry tailpipe), 93TCWOC-TP (1993 Toyota Camry without catalytic converter).

RESULTS

The approach for speciation of the Mn components employed the model compound technique. The selection of model compounds was based on knowledge of the behavior of Mn compounds in oxidative environments. The XPS and/or XAS spectra were taken on the samples and compared with spectra taken on the model compounds under the same conditions. Table 1 shows selected Mn, S, P, and O XPS parameters for the model compounds used in this study. Table 2 shows the XPS parameters for the particulate samples.

Table 1. Values of Binding Energies and Auger Parameter (in eV) for Manganese Model Compounds.

Sample	Mn $2p_{3/2}$	FWHM[a]	ΔMn 3s	Mn LMM[b]	α[c]	O 1s	S 2p	P 2p
Mn	639.0	1.40	3.4	586.5	-28.1	–	–	–
MnO	640.9	2.34	6.0	582.9	-29.8	529.8	–	–
Mn_3O_4	640.7	2.49	5.8	583.7	-29.2	529.5	–	–
Mn_2O_3	641.0	2.02	5.7	583.6	-29.0	529.5	–	–
MnO_2	641.7	2.50	4.8	583.8	-28.1	529.3	–	–
$MnSO_4$	641.8	2.39	6.3	581.2	-30.6	531.9	168.6	–
MnS	640.4	2.03	5.7	584.4	-28.8	–	160.9	–
$MnPO_4$	641.9	2.35	6.3	581.0	-30.7	531.8	–	133.9
Hureaulite[d]	641.5	2.11	6.3	581.3	-30.8	531.1 532.4	–	133.5
$Mn_2P_2O_7$	641.7	2.43	6.3	580.8	-31.1	531.5	–	133.9
$Mn_3(PO_4)_2$	641.7	2.04	6.3	581.2	-30.7	531.6	–	133.5

a) Full width half-maximum of Mn $2p_{3/2}$ peak in eV.
b) Kinetic energy of Mn $L_3M_{2,3}M_{4,5}$ Auger peak.
c) Auger parameter, $\alpha = BE + KE - 1253.6$ eV.
d) $Mn_5(PO_4)_2[PO_3(OH)]_2 \cdot 4H_2O$.

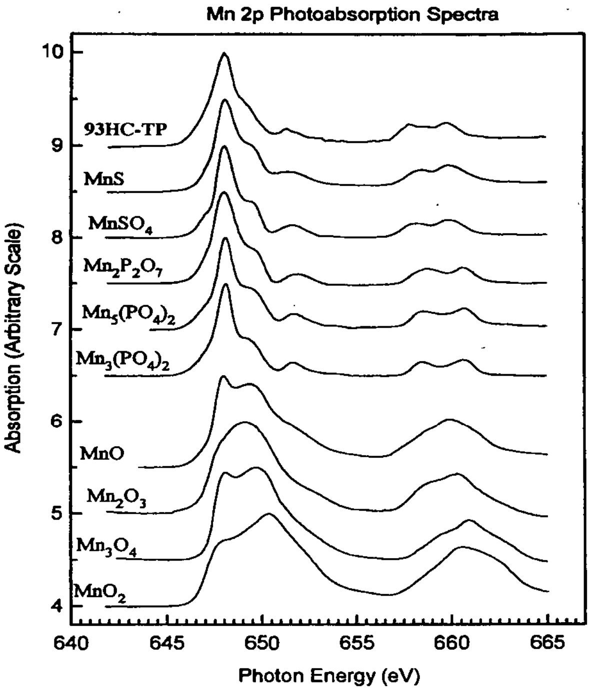

Figure 1. XAS spectra of selected Mn model compounds and the 1993 Honda Civic Tailpipe particulate sample.

Table 2. Binding Energies (in eV) of Major Elements Found in Particulate Emissions Collected on Cu and Au Foils.

Sample	Mn $2p_{3/2}$	α[a]	C 1s	O 1s	S 2p	P 2p
93HC-TP	641.8		284.5	529.9 531.5 532.8	163.4, 167.9	133.5
93HC-CO	641.7	-31.6	284.3	530.1 531.4 532.2	161.7, 162.9	133.4
92BR-TP	642.0		284.6	530.2 532.2 534.0	163.0, 169.1	133.9
93FE-TP	642.3		284.8	530.9 532.6	161.6, 163.6 166.9, 169.6	133.7
93FE-EO	641.9		284.5	532.2	161.6, 163.1	130.8 133.6
93TC-TP	641.9	-29.9	284.7	532.3	163.2, 169.4	133.6
93TCWOC-TP	642.0	-30.5	284.8	530.6 532.1 533.6	163.2, 168.1	130.7 133.7

a) Auger parameter, $\alpha = BE + KE - 1253.6$ eV.

Comparisons of the model compounds with the auto emission samples show that, in general, the particulates contain Mn phosphates, sulfates, and oxides.

Figure 1 show the XAS L-edge spectra of several Mn model compounds, one of the auto samples. Table 3 shows a summary of the XAS parameters for the model compounds, including energy shift, L_3 Linewidths and Branching ratios. Table 4 shows these parameters determined from the XAS L-edge spectra of the auto samples.

Table 3. Summary of the Mn L-edge Spectral Features for Selected Mn Compounds.

Compound	Mn Valency	$\Delta E(L_3 - L_2)$ (eV)	L_3 Linewidth FWHM (eV)	Branching Ratio $I(L_3)/I(L_3 + L_2)$
MnO_2	IV	10.1	5.5	0.65
Mn_3O_4	II, III	12.9, 11.5	4.1	0.68
Mn_2O_3	III	11.5	3.9	0.68
MnO	II	12.1	4.0	0.70
$Mn_3(PO_4)_2$	II	12.9	1.2	0.85
Hureaulite[a]	II	12.9	1.3	0.83
$Mn_2P_2O_7$	II	12.9	1.5	0.85
$MnSO_4$	II	11.9	1.3	0.85
MnS	II	11.9	1.6	0.84

a) $Mn_5(PO_4)_2[PO_3(OH)]_2 \cdot 4H_2O$.

Table 4. Summary of the Mn L-edge Spectral Features for Particulate Emissions Collected on Cu and Au Foils.

Sample	Estimated Average Mn Valency	$\Delta E(L_3 - L_2)$ (eV)	L_3 Linewidth FWHM (eV)	Branching Ratio $I(L_3)/I(L_3 + L_2)$
93HC-TP	II	11.9	1.7	0.85
92BR-TP	II	11.9	1.6	0.86
93FE-TP	II	11.9	1.8	0.84
93TCWOC-TP	II	11.9	1.5	0.85
93TC-TP	II	11.8	1.6	0.86

In agreement with the results from the XPS analyses, the predominant Mn species found in the particulate samples are Mn phosphates, sulfates, and oxides.

CONCLUSION

The XPS and XAS L-edge characterization of particulate emission samples taken from several automobiles operating with MMT in the fuels and in the UDDS mode show that the predominant Mn species are phosphates, sulfates, and oxides.

ACKNOWLEDGMENT

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