0 0 0 0 4 4 0 3 7 0 2

Submitted for publication

RECEIVED
LAWRENCE
BERKELEY LABORATORY

NOV 1 1 1975

LIBRARY AND
DOCUMENTS SECTION

LBL-4403
Preprint c.1

MANGANESE EMISSIONS FROM COMBUSTORS

A. B. Harker, P. J. Pagni, T. Novakov, and L. Hughes

September 12, 1975

Prepared for the U. S. Energy Research and
Development Administration under Contract W-7405-ENG-48

For Reference

Not to be taken from this room

LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY

LBL-4403
c.1

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

0 0 0 0 4 4 0 4 7 0 3

LBL 4403

MANGANESE EMISSIONS FROM COMBUSTORS*

A. B. Harker,+ P. J. Pagni++ and T. Novakov

Lawrence Berkeley Laboratory

University of California

Berkeley, CA 94720

and

L. Hughes

NASA, Ames Research Center

Moffitt Field, CA 94035

U.S.A.

Introduction. Undesirable emissions from aircraft, automotive and stationary gas turbine engines are produced in the combustion chamber with no significant change during subsequent flow through the turbine. These emissions can therefore be characterized by studying model combustion chamber[1] exhaust. The apparatus used has previously been described in detail[2,3]. Emphasis is therefore placed on results obtained using X-ray photoelectron spectroscopy to analyze particulate exhaust collected from a model combustor burning JP-4 with 2-methyl cyclopentadienyl manganese tricarbonyl (MMT) added in concentrations ranging from 0 to 0.25% by volume. It is desired to determine the oxidation state and physical form of the manganese after combustion as well as its effect on other particulate emissions.

Method. X-ray photoelectron spectroscopy (XPS) consists of determining the binding energy of photoelectrons expelled from a sample irradiated with monoenergetic X-rays[4]. Applications of the

---

* Supported by US-ERDA and NSF-RANN.

+ Science Center, Rockwell International, Thousand Oaks, CA 91360.

++ Mechanical Engineering Department, University of California, Berkeley.

technique to particulate analysis have been reported[5]. The electron binding energies obtained are characteristic of the element observed, with the precise value of these energies being modified by the valence electron distribution of the molecule in which the observed atom exists. The difference in electron binding energy between the elemental and molecular forms of an atom is known as the chemical shift. These shifts are correlated to the effective charge an atom possesses in a molecule and are used to establish oxidation states. The oxidation states of manganese, however, have such small chemical shifts that it is difficult to unambiguously assign an effective charge from a measurement of the chemical shift alone.

Because of this difficulty, the multiplet splitting effect was employed here to determine the oxidation state. Multiplet splitting of core electron binding energies has been observed in the photoelectron spectra of transition metal compounds and other paramagnetic species[6]. In any atomic or molecular system with unpaired valence electrons the 3s-3d exchange interaction effects the core electrons differently, according to the orientation of their spin. This causes the 3s core level to be split into two components. For an Mn^{2+} ion whose ground state configuration is $3d^5\ {}^6S$ the two multiplet states will be ${}^7S$ and ${}^5S$. In an Mn^{4+} ion having the ground state configuration $3d^3\ {}^4F$ the two spectroscopic states will be ${}^5F$ and ${}^3F$. The magnitude of the multiplet splittings should in first approximation be proportional to the number of unpaired 3d electrons. Hence the Mn(3s) splitting will be greatest for Mn^{2+} ions, and least for Mn^{4+}.

Results. A photoelectron spectrum of the exhaust particles in the binding energy range 0 to 670 eV is shown in Figure 1. The major constituents are manganese, carbon and oxygen, with

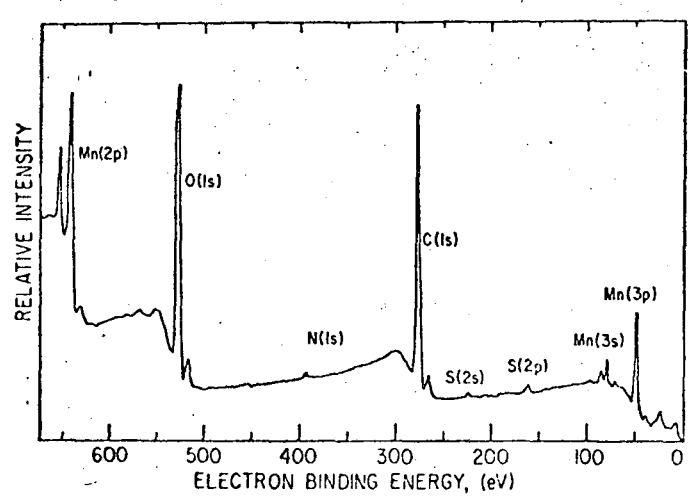

Fig. 1 X-ray photoelectron spectrum of particles emitted by a model combustor burning JP-4 with 0.25% (vol.) MMT and collected on a Nuclepore filter.

trace amounts of nitrogen and sulfur. The Mn(3p) level was used for the chemical shift measurements while the Mn(3s) level provided the multiplet splitting data. Mn(3p) binding energies have been determined for the exhaust particle samples and for the compounds MnO, Mn_2O_3, Mn_3O_4 and MnO_2. These values, corrected for sample charging using the hydrocarbon contaminant with a C(1s) binding energy of 285.0 eV, are listed in Table I. Clearly it cannot be determined on the basis of chemical shift alone whether the oxidation state is MnO, Mn_3O_4 or Mn_2O_3.

Table I. Measured Mn(3p) Electron Binding Energies

Sample	Exhaust	MnO*	Mn_3O_4	Mn_2O_3	MnO_2
Binding energy, (eV)	48.9 ± 0.2	48.8 ± 0.2	48.9 ± 0.2	49.0 ± 0.2	49.9 ± 0.2

*powered reagent grade MnO which undergoes rapid surface oxidation at ambient conditions was used[7].

The oxidation state assignment is made by examining the multiplet splittings of the 3s electron level in spectra such as shown in Fig. 2. MnF_2 is included since it is the most ionic

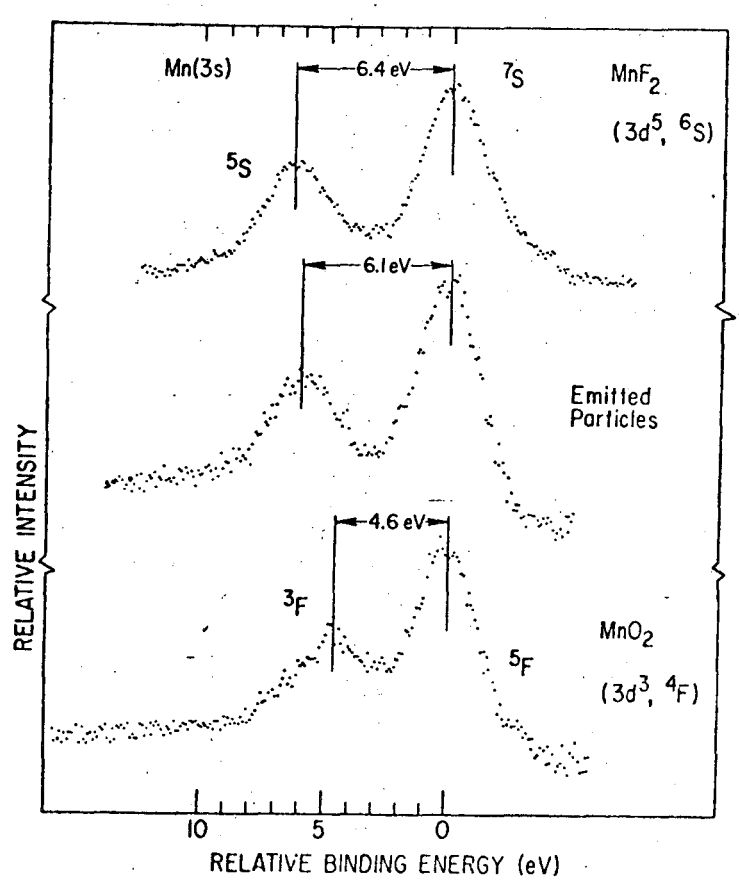

Fig. 2 Comparative X-ray photoelectron specta of 3s core levels for MnF_2, exhaust particles and MnO_2 showing the multiplet splitting of the 3s level. It is concluded that MnO is the principal manganese oxide in the emitted particles.

compound of divalent manganese and therefore its Mn^{2+} ion must exhibit the largest possible 3s multiplet splitting. Mn(3s) spectra were also obtained for Mn_3O_4 and Mn_2O_3. A summary of the measured multiplet splittings along with values from the literature is given in Table II.

Table II. Multiplet Splitting of Mn(3s)

Compound	Splitting (eV)			
	This Work	Wertheim *et al.* (Ref. 7)	Fadley *et al.* (Ref. 8)	Carver *et al.* (Ref. 9)
MnF_2 (2+)	6.4 ± 0.2	6.50 ± 0.02	6.5	6.3
Exhaust Particulate	6.1 ± 0.2	----------	-----	-----
MnO (2+)	---------	6.05 ± 0.04	5.7*	5.5*
Mn_3O_4 (2+ and 3+)	5.5 ± 0.2	----------	-----	-----
Mn_2O_3 (3+)	5.5 ± 0.2	5.50 ± 0.10	-----	5.4
MnO_2 (4+)	4.6 ± 0.2	4.58 ± 0.06	4.6	-----

*Earlier lower values for MnO (including Ref. 3) were due to surface oxidation of available analytical grade MnO. The MnO reference compound used in Ref. 7 was produced by oxidation of clean Mn in vacuo.

Based on the excellent agreement between the exhaust particulate and MnO multiplet splitting magnitudes, it is concluded that the oxidation state of the manganese in the combustor exhaust is +2 as MnO. Other Mn^{2+} compounds are eliminated by the fact that oxygen is the only negatively charged species present in sufficient concentration to stoichiometrically balance the manganese. XPS measurements of atomic ratios in the exhaust sample showed that the ratio of sulfur to carbon atoms increased from 0.047 for pure JP-4 fuel to 0.145 when the additive was used. It has been demonstrated[10] that MMT strongly influences the size distribution in the exhaust, producing many more small particles. The resulting increase in the surface area available for heterogeneous reactions could explain the increase in the sulfur to carbon ratio[11].

It is interesting to note that the manganese oxide in the exhaust particles was stable over long periods of time in the ambient atmosphere, whereas the reagent grade powdered MnO is readily oxidized. Only when heated to 500°C for 10 min. in O_2 at 100μ Hg total pressure, was the monoxide in the exhaust sample observed to form higher oxides. The stability of the particulate manganese suggests that the MnO is intimately associated with other components of

the exhaust particles. Since carbon is by far the most abundant constituent of the particles it is likely that the manganese monoxide is trapped in carbonaceous material which may form a barrier against further oxidation.

A neutron activation analysis of the exhaust samples was also obtained[12] which indicated that all the manganese added to the fuel was emitted. Knowing the amount of manganese emitted and the oxidation state as MnO, the mass of manganese monoxide emitted can be calculated. Since the total mass of particulate emissions is also measured, the mass of carbon emitted is immediately obtained. The resulting emission indices are shown in Fig. 3 as a function of additive concentration. Small amounts of the additive, less than 0.01% (vol.), decrease the

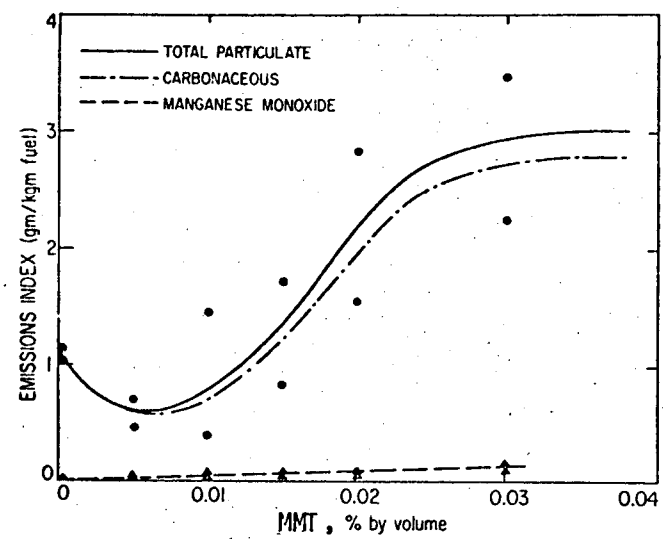

Fig. 3 Typical experimental results for the total particulate emission index. The solid line is an averaged total particulate EI. The carbonaceous EI is the difference between the total EI and the MnO EI.

emitted mass. However, at additive concentrations greater than 0.01% (vol.) both the total mass and the mass of carbon emitted increase. The carbon emission index reaches a plateau as additive concentration increases at ~1.7 gm/kgm fuel above the no additive level. A carbon deposition rate of ~1.6 gm/kgm of fuel has been reported for a similar combustor[13]. This leads to the conclusion that prohibition of carbon deposition within the combustion is the cause of the increased mass emission. Similar minimums in mass emissions at low additive concentrations have been observed for oil burning furnaces[14] and power generating turbines[15].

References

1. R. F. Sawyer, in Emissions from Continuous Combustion Systems, E. S. Starkman ed., Plenum, New York (1972) p. 243.

2. D. V. Giovanni, P. J. Pagni, R. F. Sawyer, and L. Hughes, Comb. Sci. Tech. 6, 107 (1972).

3. P. J. Pagni, L. Hughes and T. Novakov, in Atmospheric Pollution by Aircraft Engines, AGARD Conf. Proc. No. 125, NATO, London, England (1973) p. 28-1.

4. J. M. Hollander and D. A. Shirley, Annual Review of Nuclear Science 20, 435 (1970).

5. T. Novakov, in Proc. Second Joint Conf. on Sensing Envir. Pollutants, Instr. Soc. of America (1974) p. 197.

6. C. S. Fadley, in Electron Spectroscopy, D. A. Shirley ed., North Holland, Amsterdam (1972) p. 781.

7. G. K. Wertheim, S. Hutner and H. J. Guggenheim, Phys. Rev. B7:1, 556 (1973).

8. C. S. Fadley, D. A. Shirley, A. J. Freeman, P. S. Bagus and J. V. Mallow, Phys. Rev. Letters 23, 1397 (1969).

9. J. C. Carver, T. A. Carlson, L. C. Cain and G. K. Schweitzer, in Electron Spectroscopy, D. A. Shirley ed., North Holland, Amsterdam (1972) p. 803.

10. P. J. Pagni and L. Hughes, Chemosphere 1: 5, 209 (1972).

11. T. Novakov, S. G. Chang and A. B. Harker, Science 186, 259 (1974).

12. L. Hughes, "The Effect of a Manganese Fuel Additive on Air Quality," dissertation, Environ. Health Sci., School of Public Health, University of California, Berkeley, 1973.

13. E. S. Starkman, A. G. Cattaneo and S. H. McAllister, Indust. Engr. Chem. 43, 2822 (1951).

14. G. B. Martin, D. W. Pershing, and E. E. Berkau, Office of Air Programs Publication No. AP-87, U.S. Environ. Protection Agency, Research Triangle Park, N. C. (1971).

15. L. Plonsker, E. B. Rifkin, M. E. Gluckstein and J. D. Bailie, "Reduction of Gas Turbine Smoke and Particulate Emissions by a Manganese Fuel Additive" Ethyl Corp., Ferndale, Michigan (1974).

0 0 0 0 4 4 0 4 7 0 6

LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

TECHNICAL INFORMATION DIVISION
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720