LA-UR-79-1014

Conf-790447--3

TITLE: INHALATION TOXICOLOGY OF OIL SHALE-RELATED MATERIALS

AUTHOR(S): Holland, Laurence M(artin), H-4
Spall, W(alter) Dale , H-DO
Garcia, Leroy L(eopoldo), H-5

SUBMITTED TO: Health Implications of New Energy Technologies
Park City, Utah
Sponsored by Society for Occupational and
Environmental Health

MASTER

University of California

LOS ALAMOS SCIENTIFIC LABORATORY
Post Office Box 1663 Los Alamos, New Mexico 87545
An Affirmative Action/Equal Opportunity Employer

Form No. 836 R3
St. No. 2629

UNITED STATES
DEPARTMENT OF ENERGY
CONTRACT W-7405-ENG. 36

INHALATION TOXICOLOGY OF OIL SHALE-RELATED MATERIALS

L. M. Holland, D.V.M., D. W. Spall, Ph. D. and L. L. Garcia, B.S.

Mammalian Biology, Group H-4
Los Alamos Scientific Laboratory
University of California
Los Alamos, New Mexico 87545 USA

INTRODUCTION

As United States oil sources continue to diminish in the face of rising consumption, interest in oil shale as an alternative source of liquid fuel has become more intense. Production of a liquid fuel from the marlstone of the Green River oil shale formation is a complex matter and the technologies involved are in an early, trial and error, stage of development. Of the extraction techniques now extant, most involve large scale mining and rock crushing operations and the disposal of large amounts of spent material. Concerns relating to occupational health are part of the general questions that will arise in defining the regional impact of a large-scale industry. Indeed, these occupational and public health concerns and the attendant application of control technologies may be limiting factors in the economical development of oil shale.

Exposure of the work force, and to a lesser degree of the regional population to both raw and spent shale dusts, will be an important factor when consideration is given to advanced development of the resource. No threshold limit values (TLV) have been established for oil shale and its products except for the application of numbers based upon standard formulas for silica-bearing materials; (1) dust exposure becomes an important concern in the industrial environment when the relatively high free silica content of raw and spent shale (8-15%) is considered along with the complex organic materials involved (2).

The work reported here represents an effort to integrate industrial hygiene studies and chemical analyses with on-going inhalation toxicology experiments in an attempt to identify the pulmonary hazards that may arise from an oil shale industry.

METHODOLOGY

Industrial Hygiene

During the course of on-site industrial hygiene studies of an active oil shale extraction process, a number of cascade impactor samples were gathered to determine the size range of dusts associated with the process. One of these samples taken near the point where raw shale rock is fed into the retort was analyzed for total hydrocarbon content (THC) and for specific polycyclic aromatic hydrocarbons (PAH) as a function of particle size. The data derived from this sample were compared with a cascade impactor (Anderson 2000; Atlanta, GA) sample taken from exposure chambers during the course of the raw shale inhalation studies reported here.

Analytical Chemistry

The weighed filters from each stage of the cascade impactor were shake extracted with $CHCL_3$ for 72 hours, their volume reduced, and the concentrated solution injected into the gas chromatograph/mass spectrometer (GCMS). The mass spectrometer was operated in the chemical ionization mode with isobutane as the reactant gas. In this mode, the predominant ion for nearly all organic compounds results from the addition of a proton to the parent moleule. This simplified mass spectra aids in mixture analysis and also enhances the sensitivity of the GCMS. This technique, while yielding quantitative data, does not lend itself to identification of the species. However, if reference standards are available, the combination of GC retention time and mass spectroscopically determined molecular weight is sufficient to uniquely identify and quantify the compound.

In this study, twelve PAH were selected on the basis of their known behavior as environmental health hazards. These compounds are by no means the only, nor even necessarily the most abundant, PAH present in shale dust. Work is underway to identify as many PAH as possible in the shale dust extracts, and preliminary indications are that alkyl substituted PAH are quite abundant, but not as common as the unsubstituted parent PAH. Other modifications of the parent PAH such as amino, hydroxyl or aldehydeo substitutions are even more rare.

The PAH fraction is only a small portion of the extractable hydrocarbon content of shale dust. A measure of the total amount of extractable hydrocarbons is essential to characterizing shale dust. The area under any chromatographic peak is proportional to the mass of material composing that peak, therefore the total area in a chromatogram is proportional to the total volatile material injected into the chromatograph. The proportionality constant, or response factor, relating detector response to concentration is different for every compound, and can vary for the same compound depending on concentration. For this reason, an average response factor can be chosen, or the response factor for a single material at a given concentration level can be used. Instrumental factors favor the latter approach so the response factor used in this study is the response of a fifteen carbon normal hydrocarbon. Repeated analyses of a standard mixture showed the precision to be ± 3.8% relative for a 95% confidance interval, while the accuracy was 9.7% relative. The accuracy is determined by mixture composition and the precision by area measurement and sample injection technique.

Inhalation Experiments

Inhalation exposure to three kinds of shale dusts related to surface retorting technologies were initiated in late 1977. Raw Green River shale obtained from Anvil Points, Colorado, retorted shale from a vertical kiln retort and retorted shale from a solid heat transfer system are administered as aerosols at nearly identical concentrations. The shale materials are ball-milled to a fine dust, packed into a solid mass and generated with a Wright Dust Feed. Syrian hamsters have been exposed 4 h/day, 4 d/wk to concentrations of 50 mg/m^3 of respirable dusts since the beginning of the experiment. Sixty-four animals were started on exposure to each dust and the experiments are continuing at this time. Table I illustrates the experimental protocols.

Aerosol analysis has been carried out on a frequent basis throughout the course of the experiment. During the first two months, cascade impactor and cyclone samples were taken on a twice weekly basis and less frequently during the remainder of the exposures. Table II illustrates the findings of the cascade impactor studies from the raw shale aerosols. In this instance mass median aerodynamic diameter (MMAD) determinations covering a two month period averaged 2.45 μm ± .35 μm with a geometric standard deviation of 1.68 ± .14. Ninety-three percent of the sample was retained by impactor stages three or higher indicating good penetration to the deep lung [higher impactor stage numbers indicate smaller particles (3)].

RESULTS AND DISCUSSION

The results of the chemical analysis of cascade impactor samples are given in Tables III and IV and shown graphically in Figures I and II. The values in the Tables are in parts per billion (ppb) per gram of particles. For comparison, the twelve PAH have been summed and are given as PAH. The THC values are in mg/gram particles. Impactor stage numbers head the columns, with stage 0 being the largest size particles and stage 7 the smallest. In the figures, the values from the tables are shown and the dashed line is an approximation of particle size collected on the impactor stages.

The values are weight normalized, that is, the values for each stage are given in mg of hydrocarbon or ppb of PAH per gram of particles on that stage. Normal mass distributions for particles of this type tend to concentrate on a few stages, so that if the actual mass of hydrocarbon extracted were plotted, it would become apparent that the smaller particles contribute less to the total than do the more abundant particles. These smaller particles, however, are capable of penetrating further into the respiratory system and on a weight basis the hydrocarbons they contain are more accessible to leaching by body fluids.

It is important to note that the values obtained for the site collected particles and the values for the laboratory generated particles are essentially identical. This is reflected in the shape of the concentration/size curves, and in the total values obtained for PAH and THC. The summed PAH values for site collected and laboratory generated samples are 1730 ± 200 ppb and 2087 ± 200 ppb respectively. The corresponding THC values are 17.15 ± 1.66 mg/g and 16.18 ± 1.57 mg/g. These values illustrate that the inhalation studies are using aerosols which are representative of the dusts collected on site.

Most of the animals in the experiments are still alive and experiencing daily exposures; however, enough deaths have occurred in each group to afford an early look at the response of pulmonary tissues to the inhaled shale. The evidence so far indicates that raw shale dusts cause very little epithelial or fibrotic reaction and most of the particles are accumulated in macrophages (Figure 3). Retorted shales appear to elicit more inflammatory reaction with varying degrees of fibrosis; epithelial hyperplasia with extension of bronchiolar cells into proximal alveoli and thickening of intra-alveolar septa is present in all observed cases (Figures 4 and 5). The shale dusts appear as agglomerations rather than as individual particles and a peribronchiolar pattern is common to all materials. In some instances shale material has been observed in the lymphatics under the plueral surface of the lung. The changes observed in animals from the two spent shale groups are similar in every aspect, but the hamsters exposed to material from the solid heat transfer retort appear to have an earlier and more profound response. It is too early to tell if this observation will persist throughout the experiment.

The choice of a single exposure concentration has allowed comparison between the kinds of shale under study and should provide meaningful data for use in control technology development. Furthermore, the almost direct relationship between the laboratory generated aerosols and those observed during retorting operations at an active site lends relevance to the study.

The observation that chemical availability of the total hydrocarbons and the polycyclic aromatics increases as particle size diminishes is important but the organic components of these dusts should not be regarded as the only, or even the major, cause of changes in lung tissue. A silica content in the form of alpha quartz (SiO_2), of as much as 15% by weight, is certainly an important factor in any pathological changes that occur following inhalation. Finally, the chemical changes that occur during the retorting process may lead to organo-metallic complexes which have yet to be identified.

ACKNOWLEDGEMENT

This work was performed under the auspices of the U. S. Department of Energy.

REFERENCES

1) Threshold Limit Values for Chemical Substances and Physical Agents in the Workroom Environment, American Conference of Governmental Industrial Hygienists (1978).

2) G. L. Baughmam, Synthetic Fuels Data Handbook, Cameron Engineering Inc., Second edition, Denver (1978).

3) J. H. Brown *et al*., Influence of Particle Size Upon the Retention of Particulate Matter in the Human Lung, J. Am. Pub. Health Assoc. **40**:450-458 (1950).

FIGURE LEGENDS

Figure 3. Raw shale dust accumulated in macrophages.

Figure 4. Peribronchial accumulation of spent shale with proliferation of epithelial cells.

Figure 5. Extension of bronchiolar epithelial cells into area of spent shale deposition.

TABLE I

Inhalation Study Protocol

Material	Animals*	Concentration**	Frequency***
Raw Shale	64	50 mg/m^3	4 h/day - 4 d/week
Spent Shale I	64	50 mg/m^3	4 h/day - 4 d/week
Spent Shale II	64	50 mg/m^3	4 h/day - 4 d/week

---

* Syrian Hamsters 32 males - 32 females

** Respirable mass - total concentration somewhat higher

*** Minimum of 16 months

TABLE II

Cascade Impactor Samples of Raw Shale Aerosols

Date	Mass Median Aerodynamic Diameter (MMAD)	Geometric Standard Deviation (σg)
8/28/78	2.04 µm	2.00
8/29/78	2.17	1.80
8/29/78	1.96	[illegible]
8/30/78	2.25	1.64
8/31/78	1.94	1.80
9/20/78	2.89	1.50
9/21/78	2.39	1.60
10/ 4/78	2.94	1.62
10/ 5/78	2.74	1.57
10/ 5/78	2.70	1.62
10/13/78	2.80	1.65
10/16/78	1.42	1.60
10/17/78	2.55	1.61
	2.45 µm	1.68 σg
	.35	.14

Impactor Stage #	% of Material on Stage
0	.491
1	1.13
2	5.93
3	23.00
4	30.89
5	25.12
6	9.72
7	3.10
F (Back-up)	.63

TABLE III

LABORATORY GENERATED PARTICULATES

*COMPOUND/IMPACTOR STAGE	0	1	2	3	4	5	6	7	BU
NAPTHALENE	8	10	11	14	17	19	21	25	29
ACENAPTHENE	14	17	20	22	27	28	37	42	61
PHENANTHRENE	10	13	22	21	31	42	51	59	73
ANTHRACENE	11	17	26	20	35	40	48	50	74
FLUORENE	12	14	19	26	31	44	57	61	60
PYRENE	17	21	24	29	33	30	41	46	50
FLUORANTHRENE	7	10	12	11	14	17	19	20	22
CHRYSENE	4	6	6	9	11	10	12	14	13
NAPTHACENE	1	1	2	2	3	3	5	4	7
3-METHYLCOLANTHRENE	1	tr	tr	tr	1	2	2	3	4
DMBA	2	2	4	7	9	8	11	12	17
B[a]P	3	3	4	5	7	12	14	17	20
PAH	80	114	152	166	219	255	318	353	430
** THC	0.98	1.88	1.86	1.11	1.81	1.95	2.32	2.71	1.56

* ppb
** mg/g

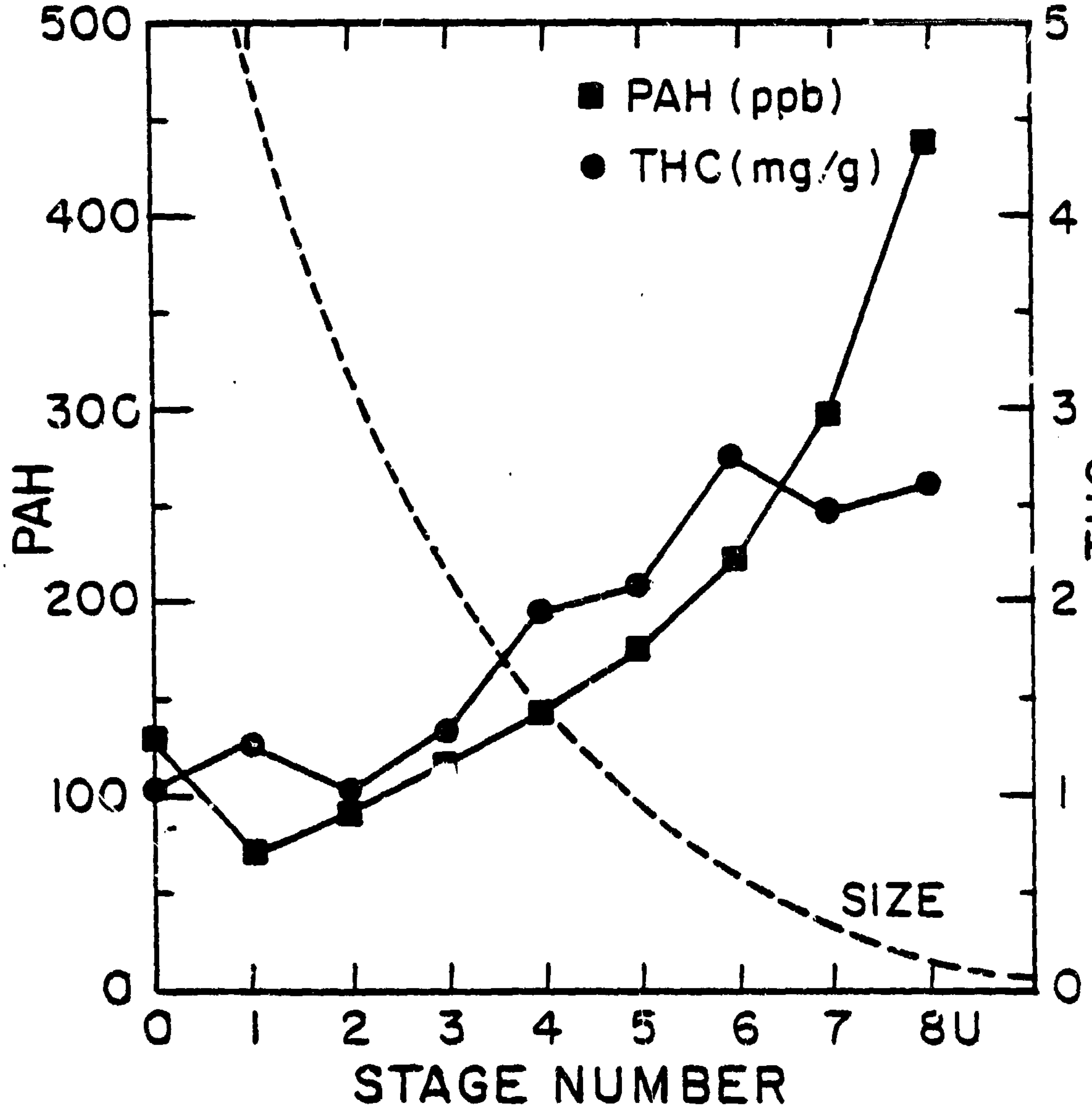
TABLE IV

SITE COLLECTED PARTICULATES

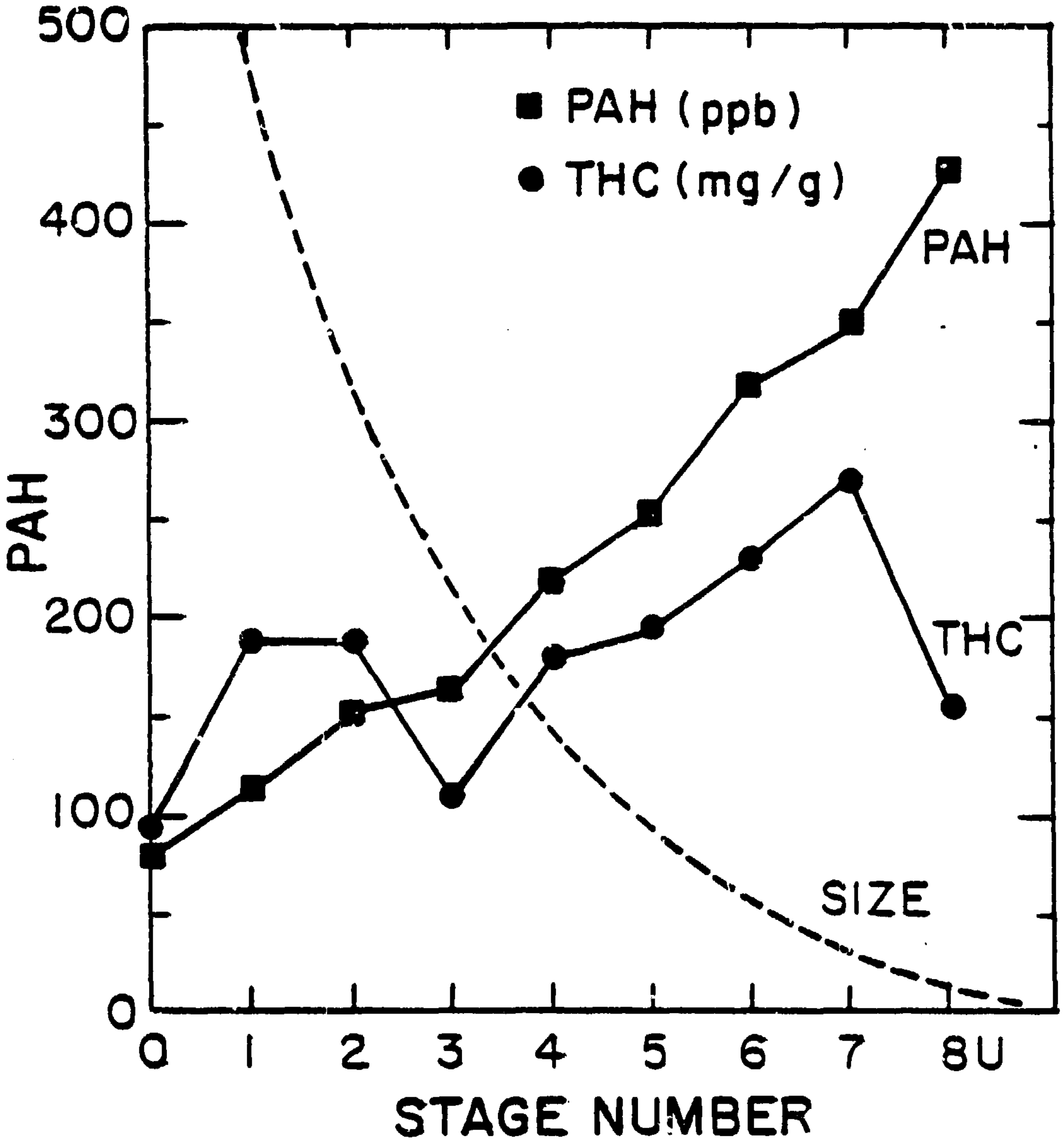
*COMPOUND/IMPACTOR STAGE	0	1	2	3	4	5	6	7	BU
NAPTHALENE	12	6	8	14	17	31	29	24	49
ACENAPTHENE	19	12	17	23	27	29	42	51	53
ANTHRACENE	27	14	14	22	22	27	30	47	77
FLUORENE	14	8	9	11	17	21	32	41	84
PYRENE	17	9	10	12	14	14	21	37	57
FLUORANTHRENE	10	4	8	7	6	5	7	9	10
CHRISENE	8	3	4	5	5	6	8	7	8
NAPTHACENE	3	2	1	tr	tr	1	2	3	3
3-METHYLCOLANTHRENE	tr	nd	nd	nd	tr	tr	1	1	1
DMBA	1	1	1	2	2	3	3	3	6
B[a]P	2	2	3	4	7	9	14	18	27
PAH	134	75	94	118	148	182	229	304	446
** THC	1.09	1.32	1.17	1.38	2.01	2.14	2.83	2.53	2.68

* ppb

** mg/g



PARAHO RAW SHALE SITE
COLLECTED PARTICULATES



PARAHO RAW SHALE
LABORATORY GENERATED PARTICULATES