

OCCUPATIONAL EXPOSURE TO FUGITIVE EMISSIONS FROM A GRAPHITE PRODUCTION OPERATION*

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In recent years, an increased awareness has arisen of the polynuclear aromatic hydrocarbon content of emissions from sources such as coke ovens, local tar heaters, or internal combustion engines. However, the fugitive emissions generated during the production of graphite have received relatively little, if any, attention. The purpose of this interdivisional study is to characterize potential PAH-containing fugitive emissions associated with the in-house production of graphite from a petroleum pitch distillate. The processes used in this production of graphite have been described in previous Carbon Conferences,^{1,2} and the work operations of concern in this study involved the chopping, grinding, and sieving of pitch, coke, or pitch-modified coke as well as certain autoclave loading and unloading operations with pitch-infused coke. Emissions from baking ovens also were monitored.

In the first phase of the study, organic fugitive emissions associated with specific work operations were characterized by a prioritized system of analysis of air sample particulates collected on air filter pads in a survey examination of the operations. The particulates collected on the air filter pads were spiked with ¹⁴C labeled benzo(a)pyrene (BaP), extracted with benzene, and the fluorescence spectra of the crude extracts were recorded. The extracts were prioritized for specific BaP analysis by a ranking according to their fluorescence intensity at a BaP emission wavelength and their particulate weight. Prioritized extracts were subjected to adsorption column chromatography and final BaP measurement by fluorescence or gas chromatography (GC). Recoveries were determined by liquid scintillation counting. The grinding of coke or pitch-coated coke produced total particulate air concentrations from <0.2 to 25 mg/m³, with BaP air concentrations from 0.23 to 0.63 mcg/m³. The chopping of pitch yielded somewhat lower emissions, with 0.92 mg/m³ of particulates and 0.12 mcg/m³ of BaP. This result may arise from the sticky, cohesive nature of the raw pitch and a lesser tendency of the agglomerated particles to become airborne. Furnace emissions appeared to be relatively low. On a 72-hr heating cycle, a bake oven produced 0.06 mg/m³ total particulates and 0.075 mcg/m³ BaP calculated as 72-hr averages. The instantaneous concentrations at any point in the heating cycle, however, could have been higher.

The single work operation associated with the highest emissions was the removal of pitch-impregnated coke blocks from an autoclave bucket. On one occasion when considerable difficulty was experienced in dislodging the blocks, the total particulate air concentration reached 9.31 mg/m³ and BaP was 2.70 mcg/m³. The residue from the infusing pitch in the bucket probably was the major source of BaP in these emissions. On a separate occasion when

the autoclaved blocks were removed from the bucket with relatively little difficulty, the total particulate and BaP levels were 0.20 mg/m³ and 0.19 mcg/m³, respectively. These data suggest that considerable variability is possible in the measured emissions associated with a given work operation. Factors contributing to such variability would include differences in how the operations were carried out as well as the usual uncertainties in reproducing an air sample collection.

Since most of these work operations were carried out in a single workroom, the greatest single source of potential worker exposure appeared to be generally restricted to that room. Hence, in the second phase of this study, emissions generated in that room during the course of a typical work shift were characterized in greater detail to estimate an overall potential exposure resulting from the various work operations carried out in a shift.

Stationary high-volume air samples were positioned at three locations within the workroom to monitor emissions which might be offered to a worker at those three sites. Air filter cassettes were changed hourly to allow an hour-by-hour measurement of emissions. The worker carried a breathing zone personal monitor to estimate actual hourly exposure. The samples were analyzed by the same prioritized system as before.

In relatively lull periods of emissions corresponding to unloading and reloading of a coking furnace, and the loading of an autoclave bucket, high-volume air samplers located at three workroom positions indicated hourly air concentrations of total particulates ranging from <0.07 to 0.6 mg/m³. In time intervals of peak emissions resulting from grinding operations and cleaning the floor and grinding equipment with a vacuum, total particulates increased to as high as 1.73 mg/m³ and BaP air concentrations reached 0.72 mcg/m³ in one location. Comparison of the data for the three samplers showed the generation and spread of emissions across the room. In one time interval, an air sampler across the room from the site of the grinding operations indicated emissions equal in concentration, but delayed somewhat in time, with those monitored by the sampler next to the grinding operation. This result suggests that the building air conditioning moved the emission cloud directly past the second sampler and that the core of the emissions cloud was undiminished in concentration. Hence, dilution of emissions may not always be assumed and worker exposure at a location somewhat removed from the actual site of emission generation potentially may be as high as at the actual generation site.

Significantly, the emissions indicated by a breathing zone personal monitor carried by a worker

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were three to five times greater in concentration than those monitored by the stationary high-volume air samplers. During lull periods of emissions, total particulate breathing zone air concentrations were $<0.1 \text{ mg/m}^3$, but during periods of peak emissions total particulates increased to as much as 5.6 mg/m^3 , and BaP air concentrations reached about 1.3 mcg/m^3 . These higher emission concentrations indicated by the personal monitor must reflect at least two factors. First, the personal monitor is closer than the high-volume air samplers to the source of emissions (*i.e.*, the production operation being carried out by the worker). Second, the worker is constantly moving and shifting about, and may come into and out of contact with localized, possibly stagnant and highly concentrated plumes or clouds of emissions inaccessible to the stationary high-volume samplers.

However, PAHs other than BaP might be present in the particulates and their presence was investigated by subjecting a 24-hr air sample to a gas chromatographic multicomponent PAH analytical procedure.³ Thirty identifiable (co-chromatography and/or mass spectroscopy) PAH ranging in ring size from 9-methylfluorene to 1,12-benzoperylene were tentatively identified. Four-ring PAHs were present in greatest concentrations. Chrysene was the most abundant PAH, with an air concentration of 1.91 mcg/m^3 (24-hr average) and a concentration in the particulates of 6.43 mcg/mg . Two C_1 -chrysene/benzanthracene/triphenylene (isomer indeterminate by MS) totaled 2.23 mcg/m^3 . A benzofluoroanthene, a five-ring PAH, was present at 0.79 mcg/m^3 . BaP was roughly estimated (because of interferences) at $<0.25 \text{ mcg/m}^3$. Some unassigned isomers of benzofluoroanthene, methylchrysene, and/or methylbenzanthracene possess carcinogenic activity, but isomer assignments, for the species in the air sample, have not yet been carried out. The remaining PAH ranged in concentrations from 0.4 to 0.01 mcg/m^3 . The total GC-volatile PAHs were estimated to correspond to an air concentration in the range of 8 to 17 mcg/m^3 (24-hr average), and to constitute 3 to 5% by weight of the particulates.

Thus, BaP made up only a small part of the total PAH in the air particulate sample, although it is the PAH of greatest popular interest.

To assess the potential inhalability of the workroom emissions, a particle size analysis was carried out on several breathing zone total particulate samples. Particulate air concentrations were found to range from 0.1 to 2×10^5 particles/l with a mass median diameter of $7.5 \mu\text{m}$, depending upon the particular grinding operation. About 70% by weight of the particles were $<10 \mu\text{m}$ in diameter; hence a significant portion were within a respirable range of particle sizes. However, only about 1% were within the 0.8 to $1.6 \mu\text{m}$ diameters corresponding to maximum particle deposition in the fine bronchioles and alveoli.⁴

An overall consideration of the results from this study suggests that graphite production from petroleum pitch can release highly localized (in both time and space), respirable, PAH-containing particulate fugitive emissions. Worker protection equipment is in use in our workrooms, and emission-containment devices are being designed. Similar measures are suggested for other laboratories producing graphite from petroleum or coal-tar pitches.

References

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