

**CHARATERIZATION OF THE LTC CATALYST:  
PERFORMANCE AGAINST COMMON AIR POLLUTANTS**

**Marcia F. Collins**

**Teledyne Water Pik  
Fort Collins, Colorado**

**For Presentation at the 79<sup>th</sup> Annual Meeting of the Air Pollution Control  
Association  
Minneapolis, Minnesota June 22-27, 1986**

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## **Introduction**

The Environmental Protection Agency has been conducting various studies of indoor air contaminants and their exposure effects.<sup>1,2,3</sup> These results and others indicate that personal exposure to specific pollutants is often significantly greater than outdoor exposure limits. Tightening up of residences for the reason of energy conservation, greater use of synthetic materials in building and furnishing interiors, tobacco smoking, and increased use of solvents all are major contributors to the deterioration of indoor air quality.

Most individuals spend up to 90 percent of their time indoors; about 70 percent is in residential and office environments. The various types of pollutants - - as particulate, or harmful gases - - have been linked to ill health effects. Currently, the most controversial issue is the effect of side stream (second hand) tobacco smoke on the non-smokers in the same environment.

As reported in an earlier paper,<sup>4</sup> Teledyne Water Pik has developed a novel room temperature catalyst (LTC) for removal of various gaseous contaminants. In particular, this catalyst oxidizes carbon monoxide (CO) to carbon dioxide (CO<sub>2</sub>) at very efficient rates. It also has shown good rates of removal of ozone, nitrogen and sulfur oxides, hydrogen sulfide, ammonia, and certain toxic components of cigarette smoke.

## **LTC Catalyst Material**

In general, the LTC catalyst consists of a solution of copper and palladium salts deposited on a porous alumina substrate. It appears that this substrate material provides a certain enhancement of catalytic activity due to its specific surface chemistry, as well as large surface area for dispersion of the LTC composition. Also a minimum of post-deposition water content, tightly held by the alumina, is necessary reasonable rates of catalytic efficiency.

## **Reaction Mechanism**

The reaction of LTC with carbon monoxide is analogous to the Wacker commercial process for producing acetaldehyde.<sup>5</sup> The oxidation-reduction cycle requires exchange of electrons between the copper and palladium metals of the complex; water is both consumed and returned to the catalytic cycle.

A simplified diagram of this reaction is shown in the Figure 1. The deposits of metal salts contain activated complexes, which create sites for selective chemisorptions of oxygen and carbon monoxide. Present theory holds that "islands" of atomic oxygen are absorbed, surrounded by carbon monoxide molecules and that the oxidation reaction occurs at the interface.<sup>6</sup> The rate of reaction is determined by the catalyst's efficiency.

## **LTC Activated Complex**

Several simple tests imply the formation of a palladium-copper complex, probably stabilized by surrounding anions. This complex is the active species, which is responsible for catalytic rates of CO oxidation to CO<sub>2</sub>.

A “catalyst” made with only the palladium salt – all else equal – was able to achieve 50 percent CO removal under standard tube test conditions. Likewise, a “catalyst” containing the two copper salts gave only 15 to 4 percent CO removal. The LTC combination of these three salts consistently removes greater than 85 percent CO.

A series of tests using stepwise additions of the metal salts constituents in various sequence ( same final composition ) clearly shows the best CO removals occur with the simultaneous deposit of the LTC composition.

## **SPECIFICATIONS FOR PERFORMANCE TESTS**

### **Tube Test for Catalytic Activity**

A one gram sample of LTC is packed in a glass tube to minimize by-pass and exposed to feed gas flow of know concentration in a single contaminant. Relative humidity in the feed stream may be varied from 10 to 90 percent, while temperature is unregulated ambient. Typical test conditions are 50 parts per million of carbon monoxide and 60 percent relative humidity at a flow rate of 500 cc/minute. The difference of CO concentration between feed gas passed over untreated substrate alumina beads versus over the LTC catalyst measures activity, which can be monitored over time. Equilibrium removal rates are the percentage of pollutant concentration lost after 6 hours. The standard deviation of 8 repetitive test results was a satisfying 2.1.

The actual amount of contaminant removed, of course, depends on physical parameters – the amount of LTC, the size and thickness of the catalyst bed, gas flow rate, length of testing, and initial concentration of contaminant CO. Time of contact with LTC reflects the former variables and is calculated from:

$$\ln (C_0/C_T) = K * t_c$$

Assuming a first-order reaction rate (oxidation of CO to CO<sub>2</sub>),

C<sub>T</sub> is the contaminant concentration at some time t.

C<sub>0</sub> is the initial concentration.

K is the reaction rate constant.

T<sub>c</sub> is the contact time.

In reality, the reaction rate also varies with the amount of surface coverage of oxygen and carbon monoxide, therefore a first order reaction scheme is a considerable simplification. The reaction constant is characteristic of catalyst material, independent of test procedures. For example, an LTC catalyst with an equilibrium CO removal rate of 93 percent, has calculated K of about 12 seconds<sup>-1</sup>.

## **Room Test of Air Filtration Appliance**

The second type of performance test measures contaminant removal in a sealed room, using the LTC catalyst filter in our filtration appliance. Filters were designed to hold 230 grams of LTC catalyst in a thin bed with minimal air flow by-pass. This test is conducted in a 1008 cubic foot stainless steel room with an initially known amount of gaseous contaminant. Air flow through the appliance was 300 CFM for the test duration of 2 hours. The standard deviation of 7 repetitive test results was and excellent 1.4

## **TUBE TEST PERFORMANCE**

### **Temperature Dependence**

The temperature dependence of the LTC performance has been reported previously <sup>4</sup>, but a brief description is included for completeness. Figure 2 maps results of a series of tests for CO removal of the LTC at various temperatures. Between room temperature and about 400 degrees C, CO oxidation ranges between 90 and 100 percent. Below about 65 degrees F, the reaction rate drops off sharply, probably as a result of increased dissipation of the heat of reaction.

In contrast, the physical adsorption of NO<sub>2</sub>, decreases as the temperature increases. Near 100 percent adsorption occurs between – 50 and + 25 degrees C, gradually decreasing to 50 percent at + 175 degrees C.

### **Relative Humidity Dependence**

The dependence of the LTC activity on relative humidity was also reported previously (4), and is illustrated in Figure 3. CO oxidation is optimum between about 25 and 70 percent relative humidity. Inadequate water present inhibits the reaction at interfaces of adsorbed “island oxygen” and surrounding CO molecules. Too much moisture fills the micropores of the alumina, effectively “drowning” these active metal deposits.

The physical adsorption of NO<sub>2</sub> is unaffected by humidity, presumably because most of the chemisorption is on the surface of the LTC/alumina bead and in the macropores. A common commercial material, Hopcalite, is severely poisoned by water vapor; it is ineffective above 10 percent relative humidity.

### **Contact Time**

One of the physical parameters which strongly affects the LTC rate of CO oxidation is the time that the contaminant is in contact with the catalyst. Table 1 shows data for contact times if 0.4 to 0.01 second, achieved by varying that gas flow rate (5 to .5 Lpm) and/or the bed depth of LTC packed in the tube. All tests were conducted at room temperature and 60 percent relative humidity with 50 parts per million (ppm) CO.

Table I  
Effect of contact time on CO oxidation

Contact Time (sec.)	Bed Depth (inches)	% Average CO Removal
0.400	1.00	84
0.200	0.50	52
0.100	0.50	30
0.080	0.40	28
0.050	0.25	17
0.025	0.25	7
0.100	0.25	2

Although equation 1 postulates a log-linear plot, the data fits a log-log curve-confirmed by regression analysis. The amount of surface coverage of the active LTC sites the CO and oxygen molecules accounts in large part for the discrepancy, as well as the fact that the oxygen-palladium bonds are weakened by the co-adsorption of the CO molecules<sup>6</sup>. Thus, the reaction conforms more closely to the Langmuir-Hinshelwood mechanism rather than a simple first order dependency<sup>7</sup>.

## ROOM TEST PERFORMANCE RESULTS

One present application of the LTC catalyst is a portable air filtration appliance for home and office environments. The LTC beads are tightly packed into a thin filter to minimize pressure drop; in the product filters LTC and activated carbon are mixed 50:50. The Instapure® Air Filtration System units used in this series of tests had LTC only (about 320 grams) and the air flow rate of 300 cfm. The contact time is thus approximately 0.02 second, or an order of magnitude less than that in the tube test. All of the following tests were conducted in a 1008 cubic foot sealed room at 40 percent relative humidity and ambient temperature. Initial contaminant concentrations are noted in each test, each of 2 hour duration. Figure 4 summarizes all of the results. The Threshold Limit Value-Short Term Exposure Limit (STEL) are recommendations issued by the American Conference of Governmental Industrial Hygienists (1983). The STEL values cited are for a 15 minute time-weighted average which should not be exceeded during a work day.

### Carbon Monoxide

A filter using 50:50 LTC to activated carbon was tested, using 30 ppm CO to begin with. The STEL limit is 400 ppm, but 30 ppm corresponds to the lower limit of the "dangerous" category established by the EPA. After 2 hours running, 55 percent of the CO was removed. Given the brief contact time, a per-pass filter efficiency of 14.6 percent may be calculated. An LTC filter removed 78 percent CO in 2 hours.

## **Ozone**

An LTC-only filter in the appliance was run in the sealed room containing 164 parts per billion (ppb) ozone (STEL limit is 300 ppb). After 38 minutes, 99+ percent was removed. Other tests indicate that the very reactive ozone molecules are decomposed to oxygen by chemisorption and subsequent interaction on the alumina surface, as well as the LTC active sites.

## **Nitric Oxide**

An LTC filter was exposed to 20 ppm NO at 300 cfm (STEL is 35 ppm). After 80 minutes, the LTC removed 20 percent, whereas the LTC/Carbon filter was able to remove 40 percent of the initial concentration.

## **Nitrogen Dioxide**

The LTC filter was exposed to 4 ppm NO<sub>2</sub> (STEL is 5 ppm). Removal was 40 percent after 100 minutes versus 100 percent removal for the LTC/Carbon Filter. The NO<sub>2</sub> molecules seem to be more tightly adsorbed to active carbon surfaces than to the LTC/alumina surfaces. As shown in Figure 2, increasing temperatures increase the rate of desorption (tube tests).

## **Sulfur Dioxide**

An LTC filter in our appliance was run in the sealed room containing 5 ppm SO<sub>2</sub> (STEL is 5 ppm). Removal of 100 percent was achieved after 90 minutes. Other tube tests<sup>4</sup> have shown that the SO<sub>2</sub> is chemisorbed by LTC active Cu(II) sites until saturation.

## **Hydrogen Sulfide**

The LTC filter was subjected to 4 ppm H<sub>2</sub>S (STEL is 15 ppm). After 60 minutes, about 100 percent of the H<sub>2</sub>S was removed. Earlier tube tests indicate an irreversible reaction of H<sub>2</sub>S with LTC which results in a gradual poisoning of the active sites. Apparently, copper sulfide is the reaction product<sup>4</sup>.

## **Ammonia**

An LTC filter in the air filtration appliance was run in an atmosphere containing 140 ppm of ammonia (STEL is 35 ppm). After 60 minutes, 58 percent was removed; 76 percent at the end of the 2 hour test. Subsequent, continuing test runs show that the catalyst is gradually saturated, with NH<sub>3</sub> removal dropping to 6 percent after 6 hours.

## Benzene

The LTC filter was exposed to 17 ppm of benzene vapor in the test room (STEL is 25 ppm). Only 8 percent was removed after 2 hours, whereas the LTC/Carbon filter was able to remove greater than 90 percent of the benzene concentration, even after each of five successive test runs. The benzene molecule is non-polar and readily adsorbed by the porous activated carbon. LTC is relatively unreactive to the benzene structure.

## Components of Tobacco Smoke

Chemical components of both mainstream and side stream tobacco smoke are present in air as particulate or aerosol and a gaseous phase. The major portion of particulate is tar, nicotine, and water; the majority of the gas phase is carbon dioxide, carbon monoxide and methane. Particulate can be removed mechanically from mainstream smoke by a paper filter (cigarettes). Table II lists some of the higher concentration constituents of tobacco smoke along with their biological effects.

TABLE II  
Some cigarette smoke gaseous constituents  
Mainstream smoke: unfiltered cigarette (a)

Gas Phase Components	Biological Activity	Wt/Cigarette
Carbon Dioxide		10-60mg
Carbon Monoxide	Toxic	10-20mg
Methane		1.3mg
Acetaldehyde	Toxic	770mg
Acetone		100-600mg
Nitrogen Oxides	Toxic	60-600mg
Isoprene		582mg
Hydrogen Cyanide	Toxic	430mg
2 - Butanone		80-250mg
Acetonitrile		120mg
Toluene		180mg
Ammonia	Toxic	80mg
Bezene	Co-Carcinogen	67mg
Acetylene		27mg
Dimethylnitrosamine	Carcinogen	10-65mg
Nitrosopyerolidine	Carcinogen	10-25mg

(a) U.S. Dept. of Health, Education and Welfare, "The Health Consequences of Smoking." 1981.

The most acute biological effect of tobacco smoke is suffered first from nicotine, and secondly from carbon monoxide. The latter markedly decreases the oxygen-carrying capacity of the blood and may impair the nervous system functions. Its effects range from inducing headaches and dizziness to implication in heart attacks and strokes <sup>8</sup>.

## **Room Test for CO from Cigarette Smoke**

The test results for CO removal from side stream cigarette smoke using the Instapure® Air Filter (AF-1) are shown in Figure 5. Two cigarettes were smoked every half-hour in a 1152 cubic foot sealed room to generate the upper curve ending at 48 ppm CO in 8 hours. The same procedure was followed while running the AF-1 appliance, which gave the center curve (32 ppm CO at 8 hours). The lower curve is for a repeat of the second test with cigarette smoking terminated after 6 hours. The air filter removes 34 percent of the cumulative CO concentration.

## **Mainstream Smoking Test**

A small filter containing 6 grams of LTC was attached to unfiltered cigarettes to test removals of mainstream tobacco smoke components. The tests were conducted by an independent laboratory and are summarized in Figure 6. Oxidation of CO is dramatic, from 17,000 ppm to 430 ppm with the LTC filter. Referring to Table II, several other hazardous compounds are significantly reduced by the use of LTC. Acetaldehyde and ammonia are diminished from 1,600 to 18 and 160 ppm more or less respectively. Likewise, methyl chloride and methyl ethyl ketone are removed in majority. Acetone and methyl alcohol are mechanically removed; several constituents are below the detection level and therefore show no change.

## **SUMMARY**

One of the important qualities of the LTC catalyst is the rapid oxidation of carbon monoxide to carbon dioxide under a wide variety of conditions. The catalytic material is a palladium-copper activated complex which reacts with various contaminant molecules through a continuous oxidation/reduction cycle. The alumina substrate enhances LTC activity with its favorable surface chemistry and very high surface area. About 10 percent surface water is necessary to facilitate the oxidation of CO. This reaction shows the log-log dependence on contact time, suggesting a Langmuir-Hinshelwood mechanism.

In the tube tests, LTC removed 90 to 100 percent of contaminating carbon monoxide in the temperature region of 20 to 400 degrees C and at ambient over a range of 25 to 65 percent relative humidity. In contrast, NO<sub>2</sub> is chemisorbed by the LTC/alumina material-the amount strongly dependent on temperature increases but independent of humidity.

Performance tests in the Instapure® Air Filtration appliance were done in a sealed room using 300 cfm air flow rate. CO was 78 percent removed, O<sub>3</sub> 100 percent removed, SO<sub>2</sub> and H<sub>2</sub>S 100 percent, NH<sub>3</sub> 58 percent, NO<sub>2</sub> 40 percent, and benzene 8 percent removed. CO from side stream tobacco smoke was 34 percent removed by the appliance. Hazardous components of mainstream tobacco smoke were effectively reduced using a small ancillary filter containing LTC.



The LTC catalyst has demonstrated excellent capability to remove an important variety of hazardous pollutant gases-which are common factors to poor indoor air quality. The Instapure® Air Filtration System incorporates the LTC catalyst in a 50:50 mixture with activated carbon to effectively remove particulate, odors, and hazardous gases at room temperature and humidities. The ability to remove hazardous gases is unique for the category of a portable air filtration equipment. The wide variety of pollutant gases that LTC removes suggests the catalytic technology is adaptable to a considerable range of commercial and industrial applications.

## REFEENCES

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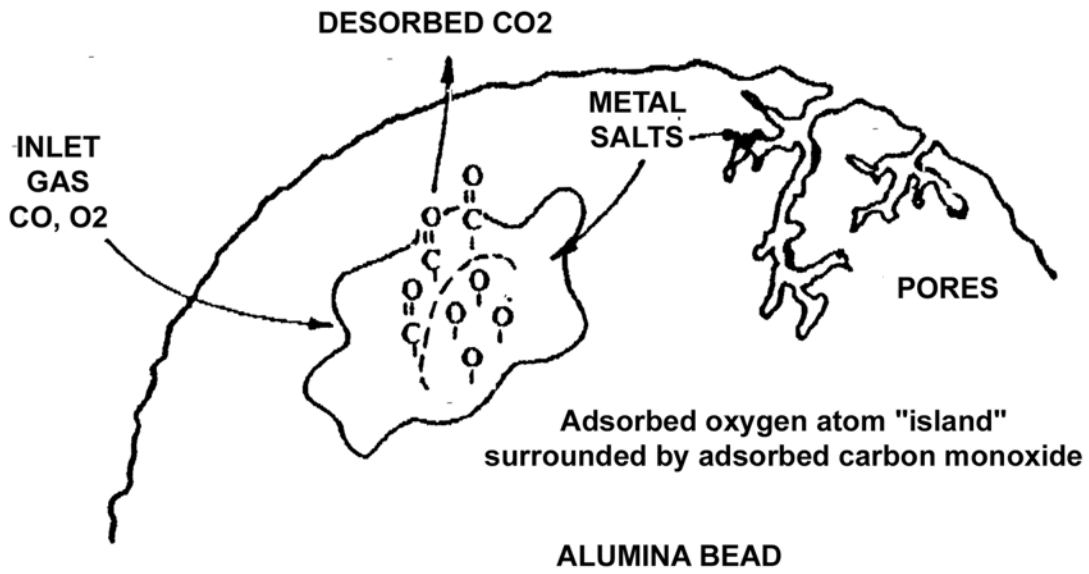


Figure 1. Diagram of Catalytic CO Oxidation Mechanism

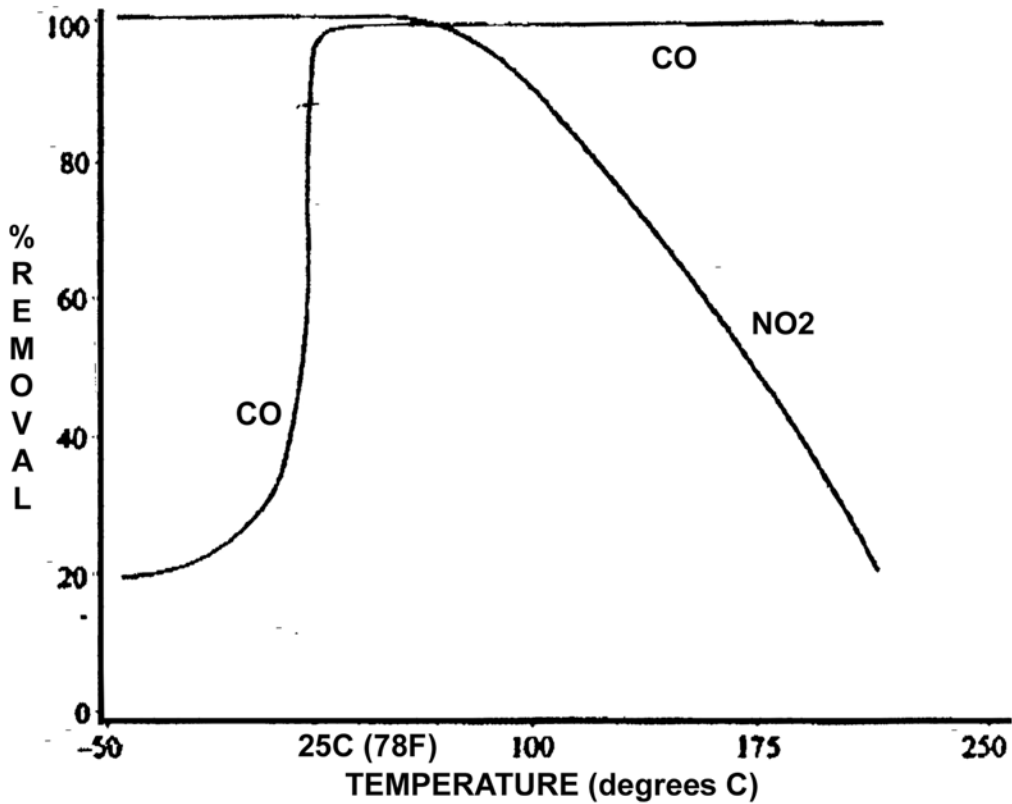


Figure 2. LTC Removal of Co and NO<sub>2</sub> as a Function of Temperature

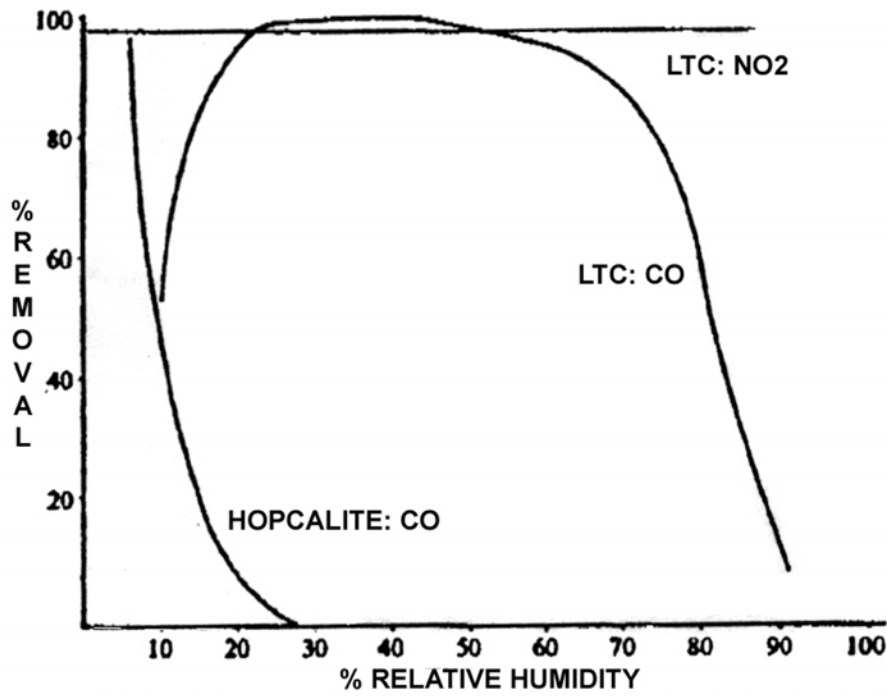


FIGURE 3. Catalyst Removals as a Function of Relative Humidity

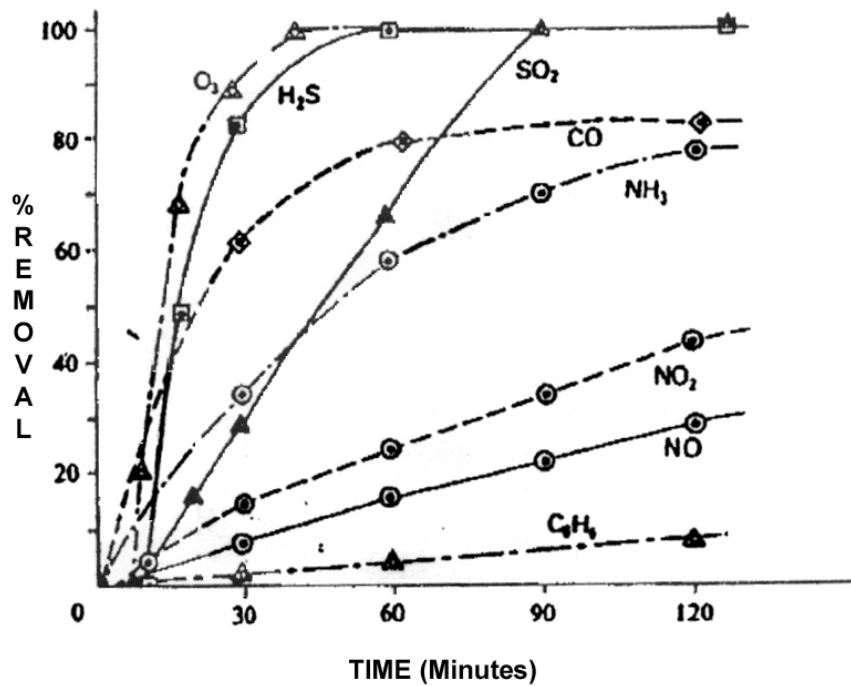


Figure 4

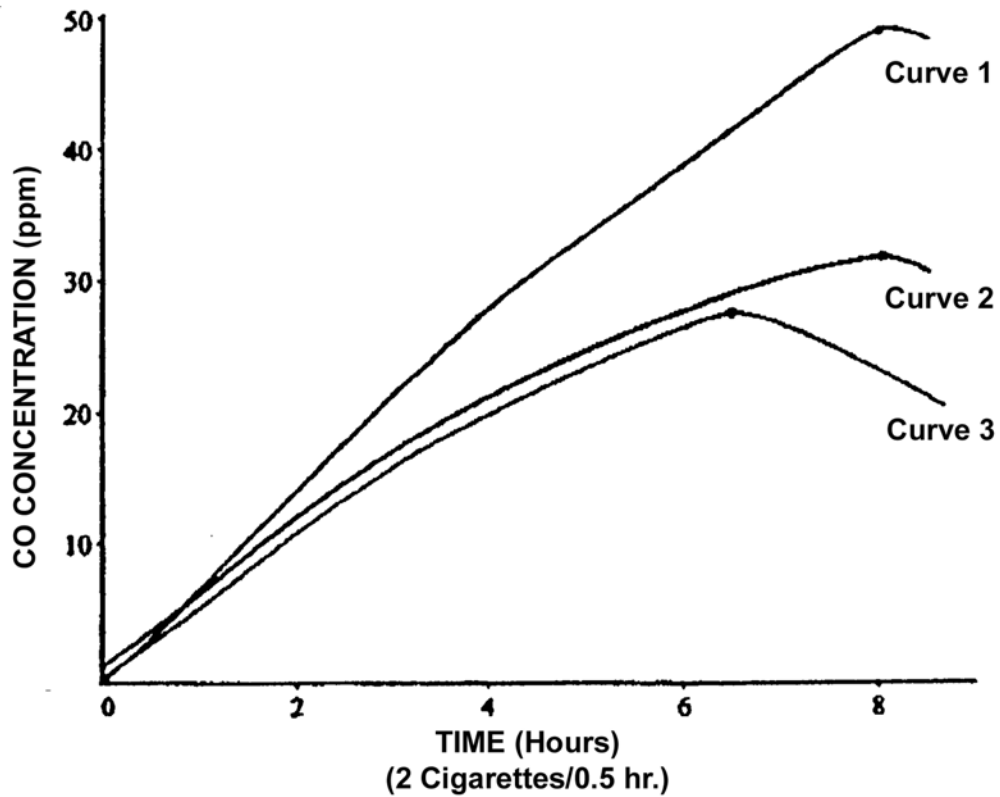


Figure 5. Room Tests of Product Filter for CO (Smoke) Removal Rate.

Pollutant	Cigarette (ppm)	LTC/Cigarette (ppm)
Carbon Monoxide	17,000.00	430
Hydrocarbons	2,700.00	600
Ammonia	1,600.00	160
Acetaldehyde	1,600.00	< 18
Methyl Chloride	550.00	84
Acetone	480.00	< 7
Methyl Alcohol	350.00	< 60
Methyl Ethyl Ketone	100.00	< 6
Hydrogen Sulfide	41.00	< 1

Figure 6. LTC Removal of Contaminants in Cigarette Smoke