# MEASUREMENT OF AUTOMOBILE EXHAUST POLLUTANT CONCENTRATIONS BY USE OF SOLID KRYPTONATES

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## ABRIDGMENT

•IT is hardly necessary to point out, in the current climate, the importance of automobile exhausts as contributors to air pollution. Inspection of both new and used cars will be necessary to ensure that, at least at periodic intervals, the emissions from a particular automobile do not exceed prescribed levels. Neither plans nor mechanisms for implementation of such an inspection program are yet established in their entirety, but some features are nevertheless clear. Suitable instrumentation for the measurement of automotive pollutant emission levels must be available and be operable by nontechnical personnel, particularly for used-car inspections. The instrumentation may be installed in fixed locations, such as inspection lanes, or may be operated for on-the-spot inspections by highway patrol cars and the like. The instrumentation should, therefore, be portable. Finally, automotive repair personnel must have instrumentation available at reasonably low cost to inform them that their repairs and adjustments have been effective.

Reasonably sophisticated instrumentation exists for the measurement of CO and hydrocarbon pollutant concentrations. Generally, these are single-channel instruments. An instrument suitable for the measurement of $NO_x$ is lacking. An instrument having the characteristics of simplicity, multichannel capability, portability, and low cost does not exist.

This paper describes the development, still in progress, of an instrument suitable for use in an inspection program whose implementation is projected for 1975.

### GENERAL DESCRIPTION

The instrument under development uses not only solid-state components but also solid-sensing materials. These sensing materials, termed Kryptonates, are solid substrates into the surface of which the radioisotope $Kr^{85}$ has been stably incorporated. Their preparation, properties, and numerous application areas have been described (1, 2, 3). All substrates used for this instrument have been prepared from small particle-sized powders, which were placed in a pressure vessel wherein $Kr^{85}$ was diffused into the surface layers at high temperatures and pressures.

Kryptonates, after preparation, can be stabilized for use at all temperatures below their stabilization temperature (1). The retained $Kr^{85}$ is released from the solid by reaction with the pollutant gas to be detected. The release rate of $Kr^{85}$ is dependent on the surface reaction rate and, hence, on the pollutant concentration. The release rate of $Kr^{85}$ resulting from reaction with the solid Kryptonate can be measured by use of a counting chamber observed by a Geiger-Müller (GM) tube.

It is possible to prepare Kryptonates from almost any solid. Judicious selection of the host solid for the Kryptonate can be made so that reaction takes place only with the pollutant to be detected. Specificity can thus be attained and a multichannel instrument constructed by use of appropriately selected sensing substrates. High sensitivity is achieved by virtue of 2 other properties of Kryptonates. $Kr^{85}$ trapped by the solid is located only in the surface layers of the solid. Only that reaction taking place at the

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surface of the solid plays a part in the gaseous detection. Further, the high sensitivity for detection of radioisotopes that is provided by conventional techniques is utilized.

$Kr^{85}$ is one of the safest and most convenient radioisotopes known. It emits, almost exclusively, a beta particle that is easily shielded. Its half-life is more than 10 years, making corrections for activity decay negligible. Because it is a rare gas, it does not enter into human metabolic processes, and significant accumulation in body tissues should not occur.

## SENSING SUBSTRATES

Suitable sensing substrates were selected (4) for the detection of automobile exhaust pollutants, specifically hydrocrabons, carbon monoxide, and $NO_x$. The substrates were responsive to the individual pollutants and nonresponsive to other pollutants present in the exhaust gases. A breadboard instrument was constructed, and the characteristics of these sensing materials were evaluated.

The breadboard instrument currently utilizes an $I_2O_5$ Kryptonate sensor operated at 350 F. A maximum sensitivity of about 80 ppm CO has been achieved in the breadboard instrument. The $Kr^{85}$ release rate is linear with CO concentration as shown in Figure 1.

For the detection of hydrocarbons, a $PtO_2$ Kryptonate operating at 500 F is used. The $Kr^{85}$ release rate is a linear function of concentration of a particular hydrocarbon in the gas stream but is a function of the hydrocarbon molecular weight as shown in Figure 2. The response is dependent on the number of $-CH_2-$ groups present in the linear hydrocarbon. For the breadboard instrument, the maximum sensitivity was about 0.5 ppm of hexane.

The sensor utilized for $NO_x$ is a hydroquinone clathrate. At room temperature, the clathrate responds to $NO_2$ but not to NO so that it is necessary to convert the NO pollutant to $NO_2$ in order to detect it. The breadboard instrument currently uses a room-temperature catalyst for the NO to $NO_2$ conversion. The maximum sensitivity for the breadboard instrument is 1 ppm.

It should be emphasized that the maximum sensitivities listed for all sensors are not the maximum achievable sensitivities. For instance, the clathrate sensing material used to attain 1-ppm sensitivity had been diluted with non-$Kr^{85}$ containing hydroquinone. These sensitivities are listed to demonstrate that much more sensitivity exists than is required if this instrument is used to monitor exhaust gases directly.

All sensing materials listed have been tested for cross interferences, and none has been detected except that the clathrate sensor responds to water vapor if the RH of the gas stream is more than approximately 90 percent. This interference is eliminated by dilution with a desiccated gas stream.

## BREADBOARD INSTRUMENT

The breadboard instrument that has been constructed is shown in Figure 3, and the flow system contained therein is schematically shown in Figure 4. This breadboard instrument has a volume of 1.25 $ft^3$ and weighs 22 lb. Future versions are expected to be smaller and lighter.

This is a multichannel instrument designed to measure the concentration of each pollutant gas sequentially. The incoming automobile exhaust stream flows through a manifold. Solenoid valves direct gases through 1 of the 3 sensing chambers containing a Kryptonate sensor. The released $Kr^{85}$ then passes through the counting chamber and is exhausted to the atmosphere through a pump. Flow rates through the instrument are approximately 1 liter/min. The $Kr^{85}$ betas in the counting chamber generate pulses in the GM tube that are fed to a simple rate-meter circuit whose output is displayed on a meter. Two rate-meter time constants are available for selection: one short-time constant to permit more rapid approximate readings and one longer time constant to permit more accurate count rate readings. For the longer time constant, decay statistics yield an uncertainty of ±1.7 percent for a full-scale reading. The breadboard instrument has been designed to provide approximately half-scale deflection for pollutant concentrations corresponding to the projected 1975 standards that have been taken as 50, 5,000, and 250 ppm for hydrocarbons, CO, and $NO_x$ respectively. The sensitivity can be easily reduced, however, by dilution with non-Kryptonate materials.

**Figure 1. Response of $I_2O_5$ Kryptonate sensor as a function of CO concentration.**

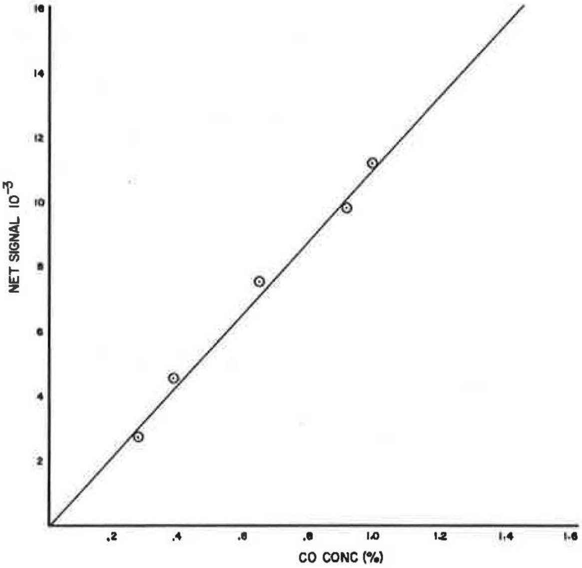



**Figure 2. Hydrocarbon species dependence of $PtO_2$ Kryptonate.**

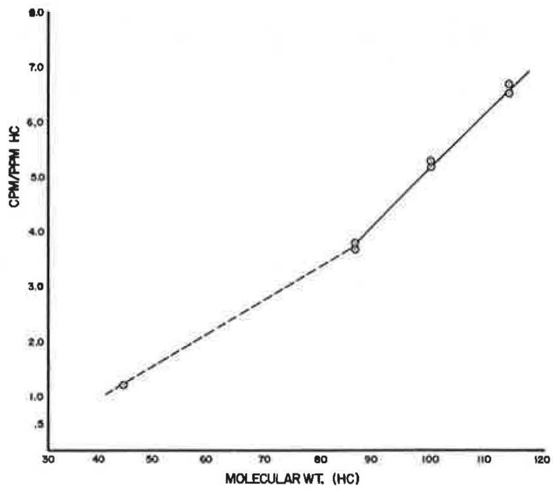
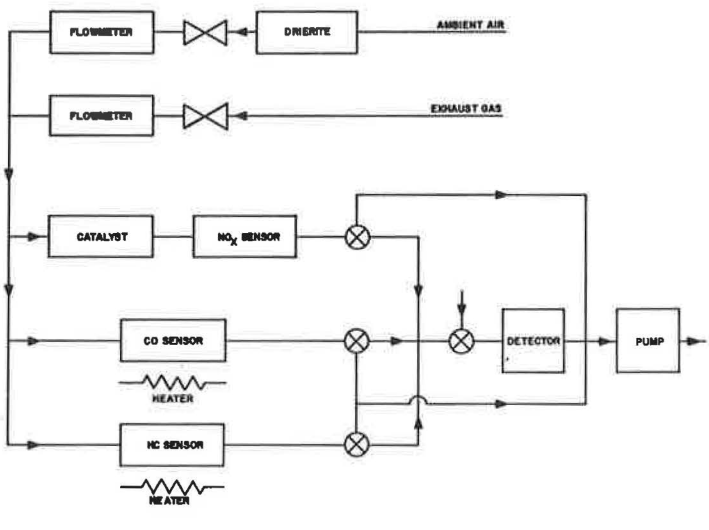



**Figure 3. Breadboard instrument for monitoring automobile exhaust pollutants.**

**Figure 4. Flow diagram of breadboard instrument.**



The breadboard was tested most thoroughly in our laboratory by the use of an exhaust stream from a 4-cycle lawn-mower engine. Indicated exhaust levels were compared with the measurements provided by an FID instrument for hydrocarbons and an NDIR instrument for CO. Satisfactory performance was obtained. Similar, but less extensive, testing with automobiles has been equally successful and promising. Poisoning of sensor response by continued exposure to exhaust gases was never observed, even with the use of leaded gasoline. Response times, measured from the time of application of a step change in pollutant concentration to the instrument inlet, are approximately 15 to 20 sec. It is expected that further design changes can reduce these response times.

Extensive testing has not, however, been performed as yet to determine the lifetime of individual sensor cells. It is calculated that each cell, containing 100 μCi of Kryptonate sensing material, could provide about 100 hours of monitoring time at an average concentration corresponding to a half-scale reading. During operation of the instrument, continuous exposure is not expected so that a 2- to 3-month operating life is projected. Such a cell would not require an individual license for the user.

## REFERENCES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