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Electrochemical ozone sensor and instrument with characterization of the electrode and gas flow effects☆

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ABSTRACT

An electrochemical ozone sensor with a new sensing composite material has been developed. The ozone sensors exhibit a strong and stable response to ozone. The responses to flow velocity and concentration have been characterized in order to develop improved ozone sensing instrumentation. Nearly an order of magnitude change in response with flow velocity is noted, along with a leveling off of the change at both the maximum and minimum flows. Operating in these regions can allow more accurate and consistent measurements.

1. Introduction

The use of ozone for sterilization and purification is increasing in both air and water applications. The advantages of ozone are threefold: *it is effective in very low concentrations*, *it can be generated directly at the point of use*, and *unlike other chemicals*, *and it leaves no residue after the source is removed* [1]. Ozone disappears from both air and water, with a half-life of 5–15 min, depending on the environment. Due to its properties as a strong oxidizer, there is concern to minimize human exposure to ozone, even very low concentrations. The United States Environmental Protection Agency has set the national ambient air quality standards at exposure limit of 80 ppb for an 8-h average [2]. The State of California has recently passed regulations requiring that all manufacturers of air purification equipment that generate ozone must certify that the products will never raise indoor levels to more than 50 ppb [3].

However, the very properties that make ozone such an effective purifying agent, its extreme reactivity/toxicity and short lifetime, also make it difficult to get accurate measurements of ozone in the breathing space. Ozone concentrations will have significant temporal and spatial characteristics even within a single room. For accurate monitoring of exposure, it is necessary to measure the ozone continuously, either at several points in a room or in the occupant's breathing zone. The options are limited for a sensor with the accuracy, small size, low-power requirements, and low cost required for widespread monitoring. UV is costly; heated metal oxide sensors are subject to critical interferences (including volatile organic compounds and humidity) [4,5]; and electrochemical sensors can also suffer from interferences and accuracy problems [6].

In spite of these shortcomings, electrochemical (EC) sensors have been widely used for ozone sensing, and, in sensitivity, they are similar to heated metal oxide (HMOX) sensors [7]. Typically, an order of magnitude improvement in sensitivity and selectivity is achieved by using UV absorption (UV) analysis for low-level ozone measurement. Improvements in EC sensor technology can combine the sensitivity and selectivity of UV instrumentation with advantages in size, portability, and cost that an EC sensor can provide [8,9]. The new KWJ EC sensor design includes a nano-structured electrocatalyst that provides excellent surface area for improved signal/noise ratio. This allows the new EC sensor to achieve the lowest of detection limits, improved response times, and stability over an extended lifetime. KWJ has designed a unique potentiostat circuit that can be powered on less than 10 mA such that the new KWJ ozone sensors will run for a several years powered by a common watch battery.

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2. Experimental

2.1. KWJ T-series sensors and pocket instrument

The T-series KWJ sensor is a 1-cm, 1-g, p-MEMS sensor (plastic microelectromechanical systems sensor) that has been commercialized for several applications (Fig. 1a). The experiments described herein utilized these three-electrode amperometric gas sensor designs [10]. Each sensor has platinum counter and reference electrodes and uses sulfuric acid as the electrolyte. Initial experiments were on sensors with sputtered gold working electrodes, and these were compared to sensors developed specifically for ozone detection that utilize a proprietary working electrode material. For reduction of ozone, the working electrode was held at a −200-mV bias with respect to the reference electrode by the low-power potentiostat.

The sensor was tested while incorporated into a very small badge-style instrument (Fig. 1b) called the "pocket ozone". The instrument continuously displays real-time ozone concentration and can report dosimetry information including the 8-h time weighted average concentration, the total exposure (ppm h), the magnitude and time of occurrence of the maximum.

2.2. Ozone sensor test fixture

Eight sensors were tested simultaneously on a board with eight potentiostats, and the signal data was recorded using a PC with data logging software. A polycarbonate box was made to channel the ozone past all of the sensors (Fig. 2). The box has a gas inlet, exhaust, and eight square holes through which the sensors are exposed to the gas flow containing ozone. The ozone mixture was safely vented after exposure to the sensors. The internal dimensions of the flow path are 1 cm high, 3 cm wide, with a path length of 18 cm.

A UV lamp ozone generator (Enmet, Ann Arbor, MI) was used to supply a fixed concentration of 5 ppm ozone. This was mixed with filtered room air controlled by a mass flow controller for dilution. The mixture flow rate was controlled with another mass flow controller and any excess was vented. In this way, the flow rate could be varied while maintaining a fixed concentration. The concentration of the gas was measured with a UV-100 ozone spectrometer (Eco Sensors, Santa Fe, NM) checked by filling a bag though a valve and at the same time pulling some of the ozone containing air with the sample draw to the UV instrument.

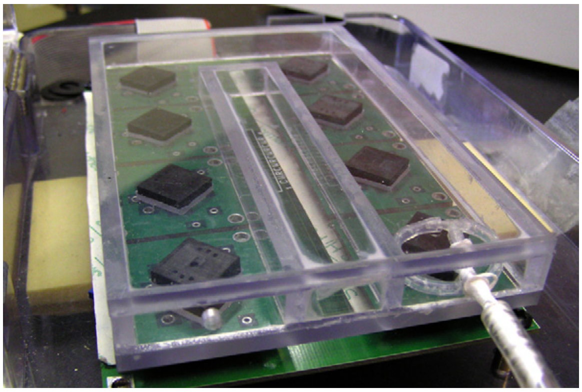

Fig. 2. Picture of test fixture box for T-series sensors. Air inlet on bottom right, exhaust bottom left. A gasket is used to seal under the sensors and raise box so the top of the sensors are nearly flush with the inside floor of the box.

2.3. Low flow pocket ozone tests

In one set of tests, the pocket ozone instruments were suspended in a rack inside a high-density polyethylene box (~3 L volume). The 5 ppm ozone in air was supplied at 1 L/min, and was sampled every 10 s by the UV-100 instrument. A small muffin (2 in. × 2 in.) fan was used to circulate the air for some of the experiments, but when used, it was not directed at the instruments.

Tests in which the pocket ozone instruments were exposed to several constant concentrations of ozone were performed in a low flow ozonated air tunnel at Eco Sensors in Santa Fe, NM. The

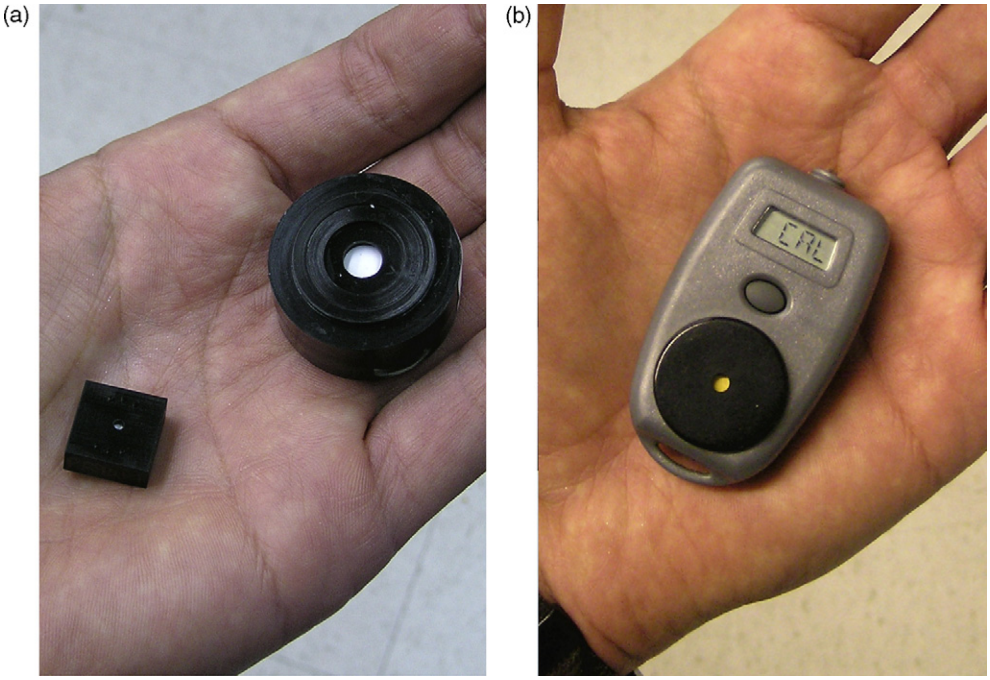

Fig. 1. (a) KWJ T-series sensor (left) and the larger R-series sensor (right) and (b) KWJ pocket instrument.