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Calibration of the QCM/SAW Cascade Impactor For Measurement of Ozone

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Abstract

The Quartz Crystal Microbalance Surface Acoustic Wave (QCM/SAW) cascade impactor is an instrument designed to collect size-fractionated distributions of aerosols on a series of quartz crystals and employ SAW devices coated with chemical sensors for gas detection. We are calibrating the cascade impactor in our laboratory for future deployment for in-situ experiments to measure ozone. Experiments have been performed to characterize the QCM and SAW mass loading, saturation limits, mass frequency relationships, and sensitivity. The characteristics of mass loading, saturation limits, mass-frequency relationships, sensitivity, and the loss of ozone on different materials have been quantified.

Introduction

The QCM/SAW flight cascade impactor is an analytical instrument composed of twelve contiguous stages that can measure eight size-segregated fractions of aerosols and detect trace gases down to sub parts per billion levels simultaneously. It is a compact, lightweight, and sturdy device that is one of the principal instruments used for the characterization of atmospheric aerosols. Since 1979, QCM crystals have been used for collecting size-segregated samples of stratospheric aerosols. [1-2] The Quartz Crystal Microbalance cascade imp actor has been used for characterization of volcanic eruption materials on the climatic effects of the stratosphere. [3]

The quartz crystal microbalance is an extremely sensitive sensor capable of measuring mass changes in the nanogram range. For a 10 MHz AT-cut crystal, the sensitivity is approximately 10^9 Hz/g. [4] A schematic of the QCM crystal shown in Figure 1. In this application, an electric voltage is applied to the piezoelectric quartz crystal (PQC) which induces a shear stress resulting in an oscillation through the body of the 10 MHz QCM crystal confined to the region between the electrodes. In the SAW device, a 200 MHz acoustic wave propagating along the surface of the crystal betwen a pair of interdigitated electrodes is induced by the applied voltage. Each individual stage contains two crystals where the upper crystal is used for aerosol or gas impaction, and the lower reference crystal compensates for frequency shifts due to temperature changes. The change in beat frequency is monitored to give near-real time measurements of the mass of deposited aerosol.

The SAW crystals have the ability to measure various gases and the mass of very small particles with a higher sensitivity. The primary application of the SAW crystal in mass-measuring instruments has been in the area of chemical sensing, in which a reactive coating applied to the surface of a SAW crystal responds specifically to a given gas through a mass change which in turn results in a frequency change. [5]

The focus of the calibration of the QCM/SAW was to determine the sensitivity, accuracy, and detection limits of the QCM and SAW crystals for ozone measurement. It was also necessary to quantify the loss of ozone through the flight stack so our data from field experiments could be accurately analyzed. The initial motivation for this work was the need for trace gas measurements to accompany aerosol measurements during stratospheric flight experiments.

Experimental Methodology

The experimental conditions for our calibration experiments simulated the sampling conditions at 18-21 km which is the altitude at which the field experiments would be performed. The calibration was performed for ozone concentrations ranging from 1-500 ppb. Two types of experiments have 'been performed for ozone; mass sensitivity/ mass loading calibration experiments and ozone loss experiments.

Preparation for a typical laboratory experiment consists of coating a crystal with a dilute (O. 1- 1.0% by mass) solution of polybutadiene in toluene. The crystal is then placed in the QCM/SAW stack where a stream of ozone is passed over the crystal for a certain length of time. A Thermoenvironmental Model 49 PS, Ozone Calibrator is used to supply the ozone to the QCM/SAW. In the ozone loss experiments, a Thermoenvironmental Model 49 C Ozone Analyzer was attached to the outlet port of the QCM/SAW stack to quantify the loss of ozone through the instrument and through transfer tubes of different materials. Both the ozone calibrator and analyzer are certified and traceable to NIST standards. The flow rate is controlled by a micrometering valve and monitored by a Matheson Model FM 1050 flow meter and exhausted with the an oiless sampling pump. Before each experiment, the beat frequency is stabilized by a nitrogen gas stream (99.995%, Potomac Airgas) directed across each of the crystals consecutively.

Mass loading is defined as the accumulation of mass onto a surface by chemical reaction, chemisorption, or adsorption or by diffusion into the bulk of the surface coating. The two primary characteristics of the mass loading properties of any crystal microbalance system are mass sensitivity and saturation limits. From the analysis of the mass loading response curves, an average mass loading is obtained for each set of experimental conditions. Total mass loadings from a series of response curves at a given flow rate and temperature produce a calibration curve. Mass-frequency relationships can be determined from this analysis. Over the course of the time that ozone is pumped across the crystal an irreversible chemical reaction occurs between ozone and the chemical coating (ozonolysis). The product of this reaction remains on the crystal causing a change in the beat frequency of the dual oscillator system. This change in frequency is monitored electronically and stored on a computer for later analysis. Mass loading characteristics for SAW crystal at 50 ppb shown in Figure 2.

Calibration experiments for the ozone loss incorporated use of the photometric ozone analyzer to measure the losses of ozone for concentrations ranging from 25-500 ppb. Two separate sets of experiments were performed to characterize the ozone loss: loss of ozone through different materials and loss of ozone through the flight stack. During these experiments, the Ozone Analyzer was attached on 1) the outlet port of the QCM/SAW stack or 2) the Ozone Calibrator connected by monel, aluminum, stainless steel, copper, and teflon in order to further characterize the possible loss processes for ozone on different materials. After stabilizing the calibrator and analyzer, ozone was passed through the tubings for one to four hours. The two lengths used were 17 $^{1}/_{4}$ in. and 58 $^{1}/_{2}$ in. with surface areas of 13.54 in^2 and 49.9 in^2 respectively. The studies helped elucidate the most efficient design for gas flow into the gas detecting stages.

In the second set of experiments, the ozone was pumped through the entire flight stack to determine the loss of ozone through the stack. The experiment ran for five hours to correspond to the flight time of an actual field experiment. Teflon was used as the tubing to deliver the ozone to the QCM/SAW stack and ozone analyzer.

Discussion and Future Directions

The primary findings obtained from this study were: 1) that the 200 MHz SAW crystal is problematic and imprecisely measures mass loading by trace gases; 2) the 10 MHz QCM crystals are sensitive enough for the measurement of stratospheric, ozone; and 3) the loss of ozone through the flight stack has been quantified, and teflon has been determined to be the best tubing for minimal ozone loss to the flight stack.

The SAW stages were originally used for gas detection. Hence, they were also first used for the calibration of ozone. Maintenance of the crystal proved to be impossible for long time or repetitive usage. The response of the SAW crystal degrades noticeably on exposure to air. The recommended cleaning procedure for the SAW crystals was ineffective and accelerated the degradation. of the SAW crystal response. The crosslinked reaction product from ozonolysis could not be removed by washing with the routine organic solvents (toluene, benzene, and methanol), and even the plasma cleaning method was insufficient to completely clean the oxygenated residue left after ozone had reacted with polybutadiene. After plasma exposure times as short as two minutes, there was observation of both electrode and crystal surface degradation. Longer or accumulative exposures resulted in even more severe damage to the SAW crystals. Observations indicate that the SAW crystals, if not pristine, are not generally reusable and further, that plasma cleaning and reuse will lead to irreversible degradation and potentially unreliable results. Due to these problems with SAW crystals, the QCM crystals became the prime candidates for the calibration of ozone on the instrument. We have found that the 10 MHz QCM crystals were sensitive enough for ozone detection down to the low ppb concentration ranges.

The QCM crystals were much more cost effective than the SAW crystals even though the cleaning method proved to be destructive to these crystals as well. To obtain accurate data, crystals had to be discarded and replaced with new crystals. Several cleaning methods were used to clean the QCM crystals after exposure. The QCM crystals were observed to have a longer lifetime and could be reused but eventually experienced performance degradation as well.

Typically, the QCM crystals were cleaned by rinsing only with the solvent of the polymer coating and then brushing it slightly with a Q-tip.

Polybutadiene was found to be selective and specific for the detection of O_3 to concentrations in the low ppbv range. This coating yielded a linear response in beat frequency as a function of the concentration under standard operating conditions. Figure 3 illustrates the mass loading response for a SAW crystal at 50 ppb. The lower bound to the sensitivity of the SAW crystals has been found to be 0.05 ng. This corresponds to ambient concentrations in the low ppb range. The mass-frequency constant is 3.0 x 10^{10} Hz/ng.

Ozone loss studies provided essential information to optimize the QCM/SAW stack with teflon being the best tubing for minimal ozone loss. Statistical analysis of the ozone loss data for teflon obtained for ozone concentrations between 25-500 ppb yielded an average loss of approximately 3%. This is in good agreement with previous ozone loss studies of the teflon coated Dasibi ozone monitors. [6] The ozone loss on stainless steel over the same range of concentrations was approximately 5%.

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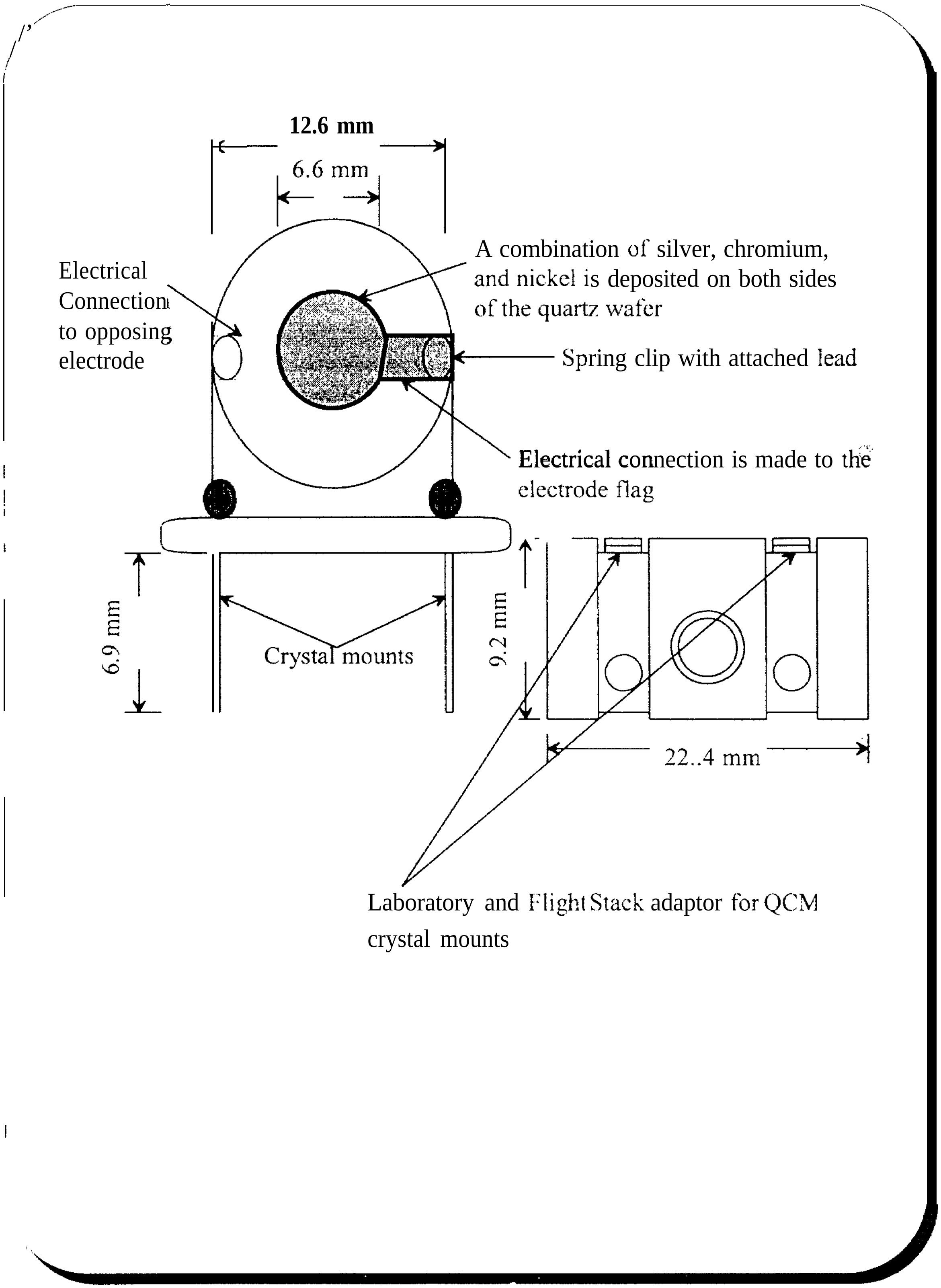

Figure1. Schematic representation of QCM crystal

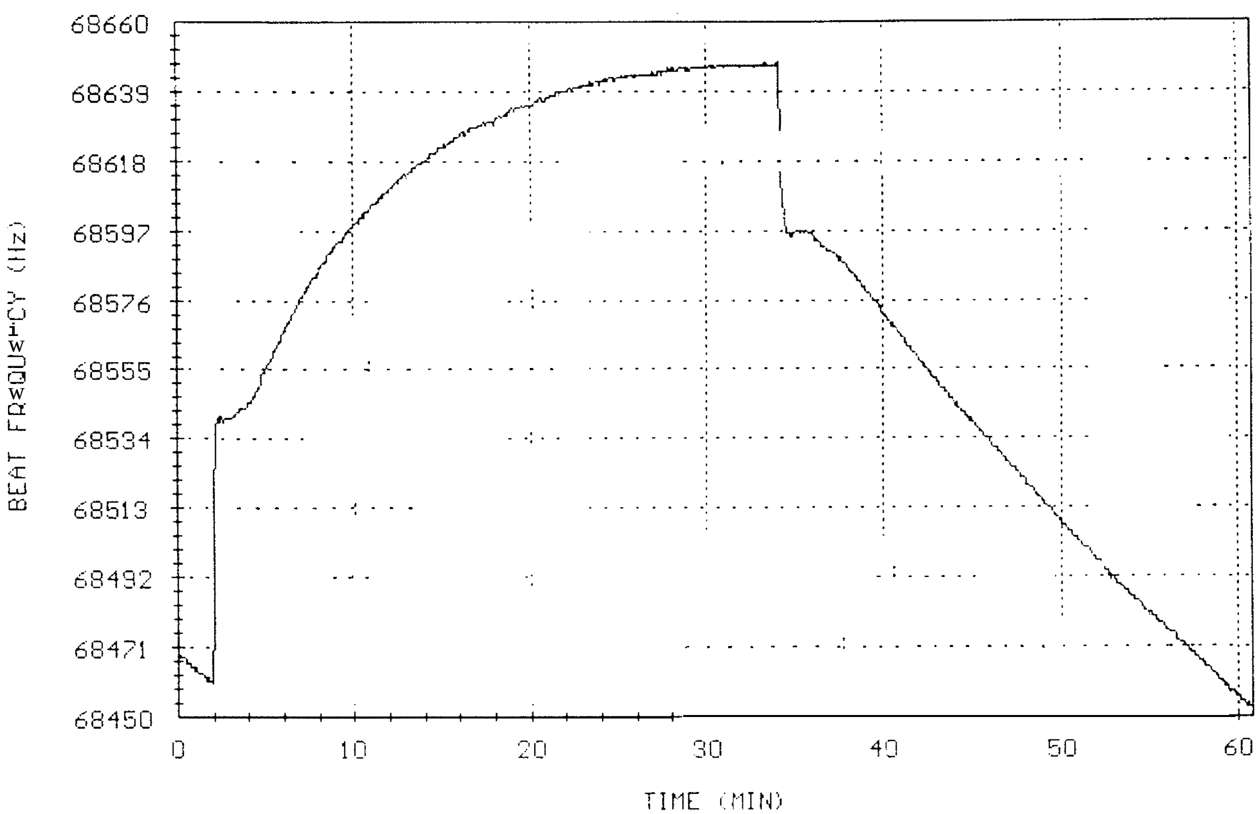

Figure 2. Response Curve of Polybutadiene with 50 ppb of ozone on SAW crystal