Evaluation of coated QCM for the detection of atmospheric ozone

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Abstract

A coated acoustic wave sensor has been developed to selectively detect atmospheric ozone. The selective detection has been assessed using a variety of coatings: beeswax, gallic acid, indigo carmine, polybutadiene, potassium iodide and sodium nitrite. Polybutadiene was the most sensitive with a limit of detection of 55 ppb. The sensitivity was improved by operating at higher harmonics and was shown to increase linearly with harmonic up to the 11th harmonic. This novel work shows that ozone detection can be improved by operating at the crystals' harmonic frequencies and in conjunction with a suitable flow rate, a potentially highly sensitive and fast response sensor can be created based on acoustic wave technology.

1. Introduction

Tropospheric ozone is an important greenhouse gas and thus influences climate but it is also a secondary air pollutant relevant to air quality. It is produced through photochemical reactions with precursor species such as nitrogen oxides and volatile organic compounds (VOCs). As precursor emissions have increased over the last few decades, ozone background concentrations have been rising in Europe (e.g. Derwent et

al.,[1]). As ozone is a transboundary air pollutant, emission controls are a global issue when air quality targets are to be met in Europe and elsewhere.[2] These increased ground-level ozone background concentrations are of particular concern as ozone can cause adverse health effects in humans and vegetation.[3] All types of vegetation can be affected, including semi-natural grasslands, forests and agricultural systems. Negative effects on crops such as reduction in yield can contribute to issues of food security and in natural/semi-natural ecosystems ozone might potentially affect biodiversity.[4]

To assess impacts on plants a flux-based metric has been developed (see e.g. Emberson et al.,[5]) which now forms the basis of some of the UNECE vegetation risk assessments. Measurements of the transport of ozone to the surface, or ozone flux, have been made by several researchers over the past 20 years (some reviewed in Wesely and Hicks,[6]). The most direct and least empirical technique employed to measure ozone fluxes is the eddy covariance method. The advantages of this approach include the measurement at a single height above the surface whilst the measured flux is the integrated net exchange with a large upwind surface area, also called the footprint, at the scale of 10^4 m^2. In order to measure ozone fluxes by eddy covariance, ozone sensors need to be both highly sensitive and fast response in order to resolve concentration differences in the small-scale atmospheric turbulent structures or eddies. To date, this has been achieved almost exclusively by the use of chemiluminescence methods.[7] These methods however suffer from three major deficiencies, namely, reliability/maintenance, calibration requirements and cost of manufacture which means that eddy covariance ozone fluxes are currently not made part of a spatially dense long-term monitoring network.

New ozone detection techniques are being continuously developed and current sensing technology for the detection of ozone are based on optochemical, electrochemical, optical or gravimetric technology all of which have advantages and disadvantages. Optochemical techniques[8] have promising limits of detection (LOD) but response times are of the order of minutes, which are not adequate for flux measurements. Electrochemical methods based on e.g. metal oxide films[9,10] have potential as they inexpensive and portable.[11] Hansford et al.,[12] have successfully used WO$_3$ sensors on an airborne platform to measure ozone profiles. Despite this, they report that the sensors respond to the oxygen as well as to ozone and they have an intrinsic response time of 30 s. More recently, a new class of nano sensors based on carbon nano tubes have been

reported by Park et al.[13] Whilst, in principle they have been shown to be sensitive down to 50 pbb, no LOD was reported and they still have time response of 100 s.

An alternative approach involves the development of low cost sensors based on acoustic wave technology that could provide both high sensitivity and sufficient response times. Such a technique, as presented here, involves the use of chemical sensors such as thickness shear mode devices coated with a recognition element. Gravimetric sensors, such as the quartz crystal microbalance (QCM) or surface acoustic wave (SAW) devices, are well suited as transducer elements for chemical sensors, being portable, rapid and sensitive. For applications in chemical sensing, a recognition element is added to the acoustic wave device capable of selectively binding or reacting the analyte to the device surface. The response of these devices is based on a change in their resonant frequency as mass is attached to the device or to the recognition element. The effectiveness of SAW devices for field based atmospheric applications has been demonstrated by Hansford et al.,[14] who have used the mass sensing principle to determine the dew point variation with altitude. Key advantages of the SAW approach are its low cost, low thermal mass, its low weight and low power consumption which are ideal for field instrument deployment.

Ozone concentrations measurements using QCM sensors have been reported by Fog & Rietz,[15] Black et al.,[16] and Wang et al.[17] All used a polymer called polybutadiene for the ozone recognition element and Fog & Rietz[15] reported a detection limit below 10 ppb of ozone and insignificant interferences from NOx, CO, formaldehyde and phenol. As the reaction with the polymer is irreversible, a useful lifetime of the coating of 80 ppb hours of ozone was found and identified as a drawback.[15] Black et al.,[16] achieved a limit of detection of 3 ppb but reported data as a 10 min running average concentration to reduce noise. Sensor response was found to be dependent on flow rate, with the higher flow rate giving a larger response. The average useful lifetime was found to range from 600-1000 ppb hours, a significant improvement to the lifetime reported by Fog & Rietz.[15] A variant of the QCM, a quartz crystal tuning fork sensor, was used by Wang et al.,[17] who achieved ozone detection at the level of tens of ppb with a sensor coating lifetime of about 120 ppb hours. The work presented here will investigate other potential reactive compounds acting as ozone recognition elements which might have suitable lifetimes for atmospheric studies. Further tests to improve sensitivity by operating the QCM at the harmonics of the resonant frequency are also performed.

2. Experimental

2.1 Quartz Crystal Microbalance

The quartz crystals used were unpolished AT-cut crystals, 25 mm in diameter, with Cr/Au contacts and operating at a fundamental resonant frequency of 5 MHz (Maxtek model No. 149211-2). The electrode area was approximately 133 mm^2 and the crystals were mounted in a Maxtek CHC-100 crystal holder. For the coating and flow rate studies, the measurement system consisted of a Maxtek PLO-10i phase lock oscillator and a HP53132A universal counter interfaced with a computer logging resonant frequencies around 5 MHz. For the study investigating the sensitivity of the sensors at higher harmonics, an Agilent E5061A network analyser was used. The spectra for the devices were recorded for several harmonics simultaneously and the resonant frequencies were determined by the minimum in insertion loss for resonant and harmonic frequencies. Prior to the application of the coating to the electrode area, the crystals were cleaned using Pirannha etch solution (1:3 v/v H$_2$O$_2$: H$_2$SO$_4$). The crystals were immersed in Pirannha etch solution for 1-2 minutes, then rinsed with deionised water and dried overnight.

2.2 Coating

Seven different coatings were tested: polybutadiene, beeswax, sodium nitrite (NaNO$_2$), potassium iodide (KI), indigo carmine, gallic acid and fluorene. All of the compounds were applied using the drop and dip-coating technique. KI was cast by applying a solution of 0.2 N KI, 0.2 N potassium acetate, 0.07 N potassium phosphate dibasic in 100 ml methanol/water (1:2 v/v).[18] The NaNO$_2$ was cast using 0.1 % NaNO$_2$, 0.2% Na$_2$CO$_3$ and 1 % ethylene glycol in 100 ml methanol/water (1:2 v/v).[19] Beeswax was cast using a solution of 1.25 g of beeswax in 25 ml dichloromethane and heating to ~40°C to fully dissolve (modified from Cape et al.,[20]). Fluorene was cast using a solution of 1 g in 10 ml of toluene. Indigo carmine was cast using a solution of 0.03 g indigo carmine in 0.2 ml ethylene glycol and 25 ml methanol/water (1:2 v/v) (modified from Scheeren and Adema[19]). Attempts were made to apply the polybutadiene using a fine bristle as described by Black et al.,[16] however this lead to unacceptable experimental reproducibility (see later) and was not used to assess the response of the

QCM. Instead, polybutadiene was cast using a solution of 0.037 g ml^{-1} polybutadiene in toluene. Gallic acid was cast using a solution of 2 g in 30 ml methanol. Gallic acid and polybutadiene coatings were also produced using a Laurell Technologies Single Wafer Spin Processor (model WS-400B-6NPP-LITE). Each coating was applied by adding 0.5 ml of solution in a pipette, before spinning the crystal for 3 seconds at 500 rpm, 3 seconds at 2000 rpm and 30 seconds at 4000 rpm. Coated crystals were stored in a glass desiccator over activated charcoal to prevent contamination from lab air and remove any traces of solvents released from the coated crystal surface.

2.3 Reagents

The reagents potassium acetate (>99 %), potassium phosphate dibasic (>98 %), sodium nitrate (>97 %), sodium carbonate (>99.5 %), fluorene (98 %), indigo carmine (85 %), hydrogen peroxide ($\geq$ 30 %, ACS reagent grade), sulphuric acid (>95 %, ACS reagent grade) and polybutadiene (M_n ~5000) were purchased from Sigma-Aldrich Chemicals. Gallic acid (>95 %) was supplied by Fluka chemicals. Potassium iodide (>98 %), sodium hydroxide (Analar) were supplied by BDH chemicals. All the solvents were of analytical grade from Sigma-Aldrich Chemicals. Refined, yellow beeswax was supplied by ACROS Organics, Geel, Belgium. All reagents and solvents were used as supplied.

2.4. Experimental set up and sensor evaluation

Ozone was generated by passing a flow of dry air (BOC gases) through an ozonizer (Science Pump Corporation ECC Ozonizer TSC-1) and pumped across the QCM surface using an all Teflon ozonesonde pump. The coating tests and runs at higher harmonics were all conducted at the constant flow rate of the ozone sonde pump of 224 SCCM. In the flow rate study the varying flows were controlled by 0 – 100 SCCM calibrated mass flow controllers (Type 1179A MKS Instruments) which controlled the flow through the QCM reaction cell. Any exhaust flow was passed through a KI O_3 scrubber and vented into the laboratory. The ozonizer was calibrated via the absorbance of ozone at 254 nm (σ = 1.15 $\times 10^{-17}$ cm^2 molecule^{-1}) using an UV/visible Spectrometer (Perkin-Elmer Lambda 25) in an optical-path length of 5.2 cm.

For all experiments, the coated quartz crystals were placed into the crystal holder and ozone-free air flowed over the crystal until a stable background was obtained. Then,

either different concentrations of ozone (0 – 825 ppb) at a fixed flow rate or a constant concentration at a range of flow rates (10 – 100 SCCM) flowed over the coated QCM. The frequency was recorded until a stable response without further frequency shift was reached. The lifetime of the coating was assessed by monitoring the frequency change for a period of 4 – 20 hours. After each run the coated quartz crystal was cleaned in Piranha etch solution and the experiment was repeated.

3. Results and Discussion

3.1 Coating tests

Ozone is an important oxidant and the selected coatings utilise the oxidative properties of ozone to generate a mass change in the applied coating which can be detected by the QCM. Sodium nitrite, indigo carmine and KI have been utilised in ozone passive samplers.[18,21,22] Ozone is known to oxidise aromatic rings in the gas phase via addition to the aromatic ring[23] and is exploited in the fluorene and gallic acid coatings. Furthermore, addition of ozone to gallic acid is utilised in the widely used chemiluminescence instrument developed by Guesten et al.,[24] based on the reactive reagent development by Sahand et al.,[25] and Speuser et al.[26] Ozone will also oxidise unsaturated hydrocarbons via addition to the double bond[27] and this property is utilised in the beeswax and polybutadiene coatings. Furthermore, beeswax has been shown to be an ozone-reactive wax in a recent study by Cape et al.,[20] as it contains unsaturated long chain hydrocarbons. Finally, polybutadiene has also been shown to be a promising coating for the detection of atmospheric ozone by a coated QCM (e.g. Black et al.,[16]).

Figure 1 shows the frequency shift in response to addition of ozone (for compounds $NaNO_2$, KI, polybutadiene and gallic acid). For each coating there is an initial large drop in frequency, which quickly equilibrates to produce a stable frequency shift ($\Delta f/\Delta t$), which eventually plateaus as, presumably, as all of the active sites within the coating have reacted away. Of the seven coatings examined, only fluorene failed to display any response on addition of ozone. The effective lifetime of the coating was estimated by taking the Δt from the start of ozone exposure until the reaction plateau, and normalising for the ozone concentration of exposure giving an expression of lifetime in ppb hours. Figure 2 shows a typical plot of frequency shift Δf vs. ozone concentration $[O_3]$ for a gallic acid coated QCM. The slopes, which represent the

sensitivity of the coated QCM towards ozone, are summarised in Table 1. The limit of detection (LOD) is calculated as the change in frequency above pre-ozone exposure background noise at the 3σ level (Table 1).

The passive sampling compounds, i.e. sodium nitrite, indigo carmine and potassium iodide all responded to ozone. These compounds displayed a large initial drop in signal and reached an equilibrium response after 30 s. The reagents crystallised on the QCM surface during the coating procedure and it was thus difficult to reproducibly and evenly coat the QCM surface, so these compounds were excluded from further studies. Reproducibility can also be an issue in passive samplers and the reproducibility of the method for indigo carmine of 5 ± 4 %[21] can be described as inadequate. KI has previously been used as an active coating in HSGFET gas sensors[27]. However at RH above 65% KI underwent agglomeration on the sensor surface and the sensor signal was lost, limiting the applicability of the sensor to a narrow window of humidity conditions. Fuchs et al.,[27] also suggested KCl could be used as an active coating, but the sensitivity was shown to be reduced by a factor of ~2. Given this reduction in sensitivity and that KCl would also crystallise on the QCM, other alkali halides were not investigated.

The aromatic gallic acid coating had a long effective lifetime yet a low sensitivity on exposure to ozone and fluorene did not show any response on exposure to ozone. By analogy with the gas phase reactions with ozone, fluorene reacts very slowly, and only an upper limit has been reported[28] yet hydroxyl substituted alcohols aromatics increase the reactivity. For instance toluene has a gas phase ozonolysis rate coefficient of 3×10^{-21} cm^3 molecule^{-1} s^{-1}, yet o-cresol, n-cresol, p-cresol have gas phase ozonolysis rate coefficients of 3×10^{-19}, 2×10^{-19} and 5×10^{-19} cm^3 molecule^{-1} s^{-1} respectively. The enhanced reactivity of gallic acid in comparison to fluorene could explain why only gallic acid produced a detectable change in mass on exposure to ozone. The effective lifetime of gallic acid coating was reduced significantly when applied using the spin coating technique in comparison to the dip coating technique (see Table 1), presumably as less mass is added to the QCM.

The beeswax coating and polybutadiene coatings were the most sensitive coatings on exposure to ozone. Beeswax is a mixture of organic compounds such as unsaturated and saturated fatty acids, alcohols and esters and polybutadiene contains unsaturated alkenes. Both presumably produce a mass change on reaction with ozone via addition to

the carbon double bond. In the case of polybutadiene this has indeed been shown by Wang and co-workers who analysed Fourier Transform Infrared (FTIR) spectra of a polybuatdiene film before and after ozone exposure. Additional oxygenated functional groups (e.g. C-O single bonds) were identified in the oxidised polybutadiene film.[17] Once again, analogous to gas phase reactions ozonolysis of alkenes is three orders of magnitude faster than reaction with aromatic hydrocarbons.[29] Thus one would expect these coatings to show the best sensitivity on exposure to ozone. From the data presented in Table 1 it is clear that the polybutadiene coated QCM is the most sensitive towards ozone. Beeswax does not react as fast as polybutadiene as it is not a pure unsaturated hydrocarbon. Our reported LOD is 55.8 ppb (for S/N = 3) and is a factor of 20 less than the 3 ppb (for S/N = 3) reported by Black et al.,[16] and our effective lifetimes are 97 ppb hours as opposed to the several hundred ppb hours reported by Black et al.[16] It is unclear as to why such a discrepancy exists. One possible explanation is that Black et al. (2000) coated the QCM on both sides whilst we could coat just one side of QCM. Black et al.,[16] used "a fine bristle brush" to apply the polybutadiene coating which was done for the coating study, but it resulted in a large scatter in sensitivities between runs, i.e. different coatings as shown in Figure 1, which was improved upon in the flow rate and higher harmonics study by generating thinner and more even coatings using the spin coating technique.

3.2 Flow rates

The response of the polybutadiene spin coated QCM to altered flows was also tested and all tests were performed at one concentration, 165 ppb. The frequency shift ($\Delta f/\Delta t$) of the crystal as a function flow across the QCM was evaluated and is summarised in Table 2 and Figure 3. The polybutadiene coating shows a distinct positively linear correlation with the increasing flows from 10-100 SCCM. This is in agreement with the findings of Black et al.,[16] and indicates that polybutadiene is mass transfer limited, not reaction limited in its response to ozone and therefore greater supply of ozone flow to the crystal surface creates a more rapid response. However, the lifetimes are inversely correlated with sensitivity which is an aspect that has to be considered when aiming to deliver a sensor package for field use. Background noise levels are found to be significantly reduced compared to those in Table 1, which is due to the improved polymer film produced by the spin coating technique. This reduction in noise impacts on the LOD which is also greatly lowered (Table 2).

3.3 Harmonics

Sauerbrey[30] first reported the relationship between frequency shift in a quartz resonator and the mass of substance deposited on the surface. Based on Sauerbrey's equation, the relationship for a rigid mass layer is modified for harmonic frequencies as follows,

$$\Delta f = -\frac{2nf_0^2 \Delta m}{A(\rho_q \mu_q)^{0.5}}$$

(1)

where f_o is the resonant frequency of the device , n = the harmonic of f_o, Δf is the change in frequency obtained from an increase in mass Δm, A is the sensing area, ρ_q is the mass density of the quartz and μ_q is a shear modulus substrate-dependent constant. Equation 1 shows that it is possible to increase the sensitivity of the coated QCM sensor by operating at higher harmonics. The network analyser was used to investigate the harmonics n = 1-11 for polybutadiene coatings only. Figure 4 shows the frequency shift of the QCM as a function of harmonic, and the frequency shift is indeed a linear function of the harmonic, i.e. the Sauerbrey model holds. Also included in Figure 4 is a plot of the normalised frequency shift $\Delta f/n$ is displayed for the overtone orders 1-11. Within experimental error $\Delta f/n$ (n, the overtone order) is the same on all harmonics. As suggested by Goubaidoulline et al.,[31] this scaling of the frequency shift Δf with overtone order, n, is characteristic of the Sauerbrey equation. The Sauerbrey relationship assumes that the fractional decrease in frequency is equal to the fractional increase in mass, i.e. it ignores all viscoelastic effects. Our results seem to suggest that the Sauerbrey relation is obeyed. As with the work of Goubaidoulline et al.,[31] there is a slight dependence of the normalised frequency shift $\Delta f/n$ with harmonic, however, it must be stressed that within experimental errors there is no dependence on harmonic and thus it may be assumed that viscoelastic effects are indeed negligible, which in the context of sensing, this is a highly desirable situation.

The work presented in this paper shows that it is possible to increase the sensitivity of the QCM by operating at higher harmonics. However, at the higher harmonics (n = 9 & 11) the reflected power of the device is greatly reduced and hence the signal cannot be distinguished from the noise unambiguously, as is reflected by the large error bars.

Whilst operation at $n = 9+$ would not improve ozone detection, running a 5MHz QCM at higher harmonics ($n = 3$-7) is an effective method of increasing sensitivity without using more delicate QCMs with higher resonant frequencies f_0 which are achieved by thinner crystal cuts. To the best of the authors' knowledge this represents the first detection of gas phase species using a QCM operating at higher harmonics. This novel work shows that ozone detection can be improved by operating at the crystals' harmonic frequencies and in conjunction with a suitable flow rate, a potentially highly sensitive and fast response sensor can be created based on acoustic wave technology. The issue of a limited lifetime, whilst maintaining a sufficient sensitivity, remains a concern if such a sensor is to be used in atmospheric studies. However strategies that extend lifetimes by e.g. diluting the sample air could be employed to improve the sensor package.

Conclusion

In this work we have demonstrated that a coated quartz crystal sensor can be used to detect ozone with a LOD of tens of ppb. Seven different reactive compounds were tested as coating materials and the most reactive compound, polybutadiene, was found to be most suitable for ozone sensing at atmospheric levels. The sensitivity of the device was enhanced by operating at higher harmonics ($n = 1$-11) by an order of magnitude. It was also shown that further improvements in sensitivity can be achieved by using high flow rates. The limitation from the short coating lifetime was considered to be extendable by diluting the sample air. Alternatively, the use of surface acoustic wave devices (SAW) with a dominant shear horizontal polarization may be employed that will extend the range of operating frequencies to over 1 GHz.[32] By increasing the resonant frequency of the sensor, the mass sensitivity of the acoustic device would be equally increased. The implementation of these enhancements should provide an increased sensitivity, allowing the detection of low levels of ozone. The work presented in this paper shows that coated QCM have the potential to be utilised for flux work, however the effective lifetime of the coating preclude them from replacing currently used chemiluminescence sensors at the moment.

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Figure and Table Captions

Figure 1. Response of coated QCM on exposure to ozone, A. for five runs of polybutadiene upon exposure to 165ppb of ozone B. for KI upon exposure to ----165 and ......825ppb of ozone C. for $NaNO_2$ upon exposure to 165 (added at 1 min) and 825 (added at 150 min) ppb of ozone and D. for gallic acid on exposure to 825 ppb of ozone.

Figure 2. A typical calibration plot of the response of the QCM vs. [ozone] for a gallic acid coating. The errors represent 1 σ from a linear least squared fit of ($\Delta f/\Delta t$) on exposure to ozone.

Figure 3. A plot of the change in sensitivity ($\Delta f/\Delta t$) vs. flow rate (SCCM) of polybutadiene coated QCM on exposure to 165ppb of ozone. The errors represent 1 σ from a linear least squared fit of ($\Delta f/\Delta t$) on exposure to ozone.

Figure 4. A box and whisker plot of sensitivity ($\Delta f/\Delta t$) and the normalized frequency shift df/n for a polybutadiene coated QCM as a function of Harmonic. Where the whiskers are the 5th and 95th percentile.

Table 1. A summary of the lifetime, sensitivities and Limits of Detection (LODs) of the coating studied in the work operating at fundamental frequency of the QCM. § Lifetime calculated for cast solution, †Lifetime for dip coated and ‡ Lifetime for spin coated.

Table 2: A summary of the change in response of a polybutadiene coated QCM operating at the fundamental to varying flows. The errors represent 1 σ from a linear least squared fit of ($\Delta f/\Delta t$) on exposure to ozone.

Table 1

Coating compound	Lifetime (ppb hours)	Sensitivity (Hz min^{-1} ppb^{-1})	LOD (ppb)
Polybutadiene	97.2§	-1.579	55.8
Beeswax	14.8	-0.047	154.8
Sodium Nitrite	>3264	-0.001	622
KI	794.8	-0.640	257.8
Indigo Carmine	45.6	-0.003	165.2
Gallic Acid	2778.89† 82.7‡	-0.013	2756.8
fluorene	N/A	0	N/A

Table 2

| Conc (ppb)	Flow (sccm)	Mean Slope (Hz min^{-1})	Error (Hz min^{-1})
165	10	32.27	9.25
165	15	57.87	5.11
165	20	83.17	5.56
165	50	108.93	3.96
165	75	141.14	2.94
165	100	160.93	2.29

Figure 1

A
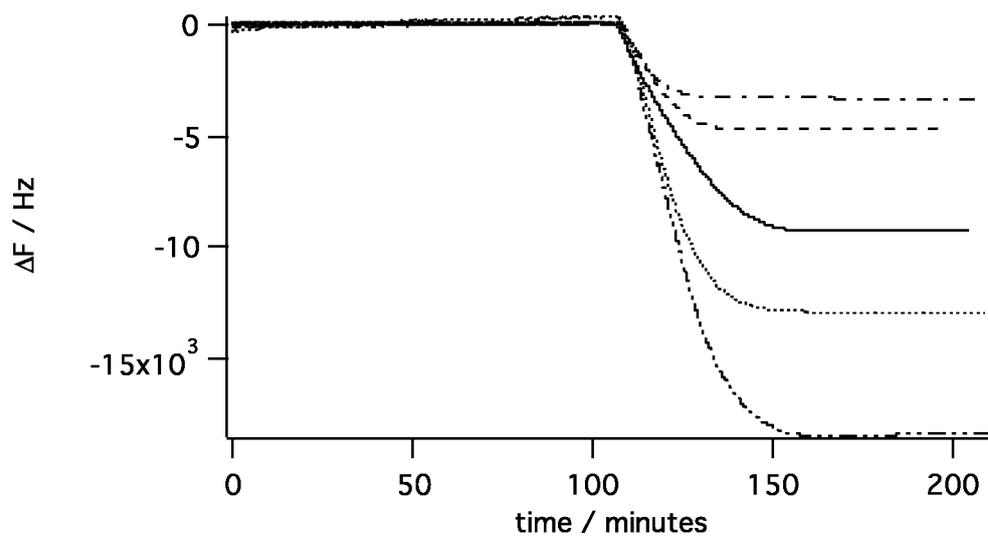
B
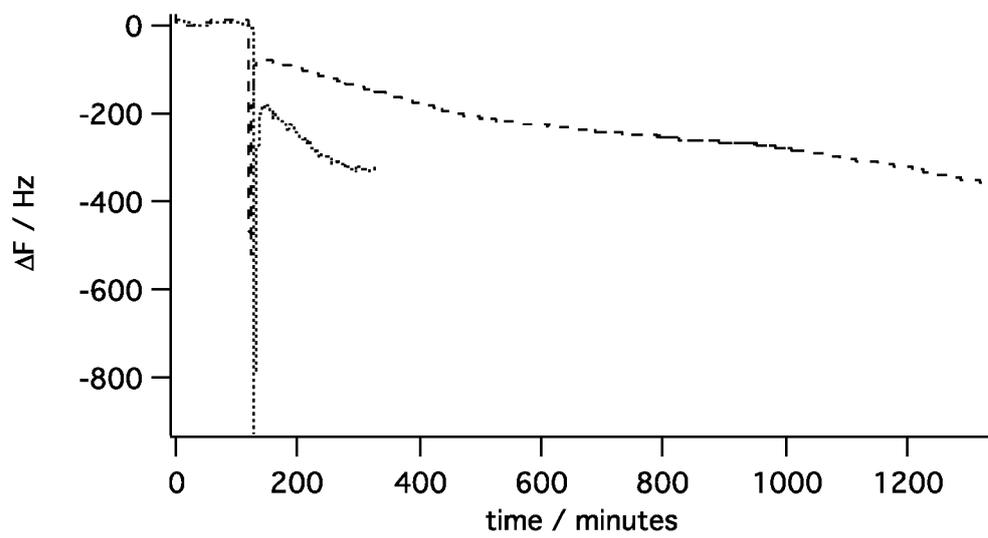
C
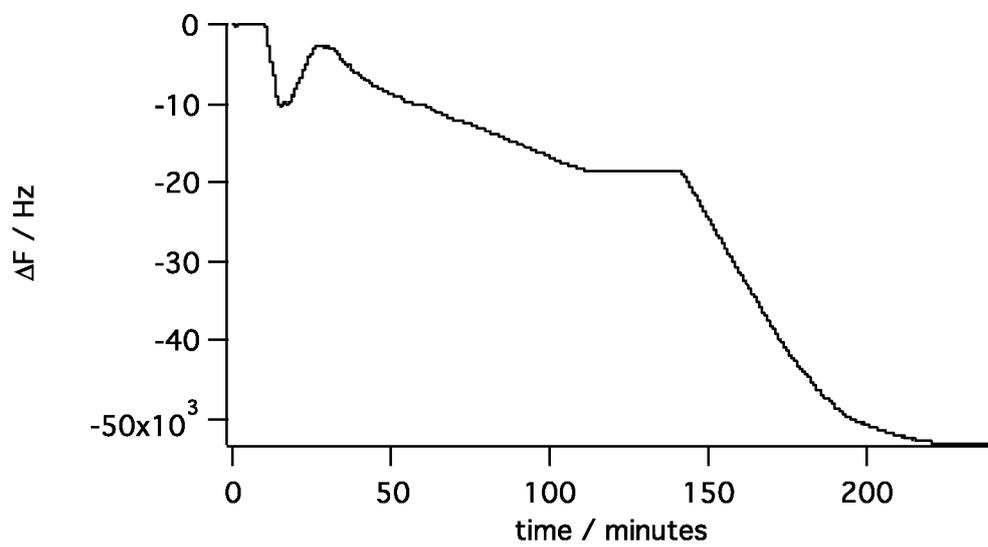
D
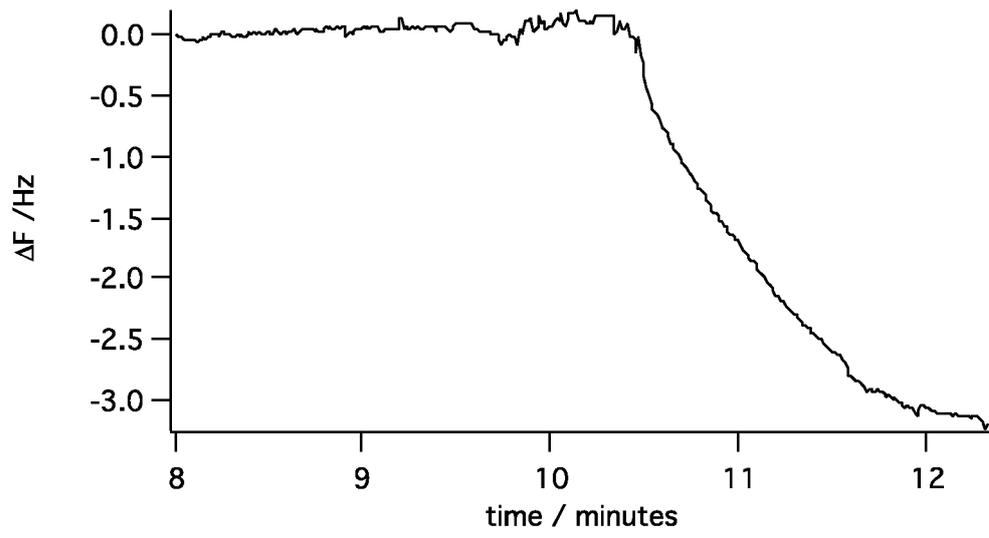
Figure 2
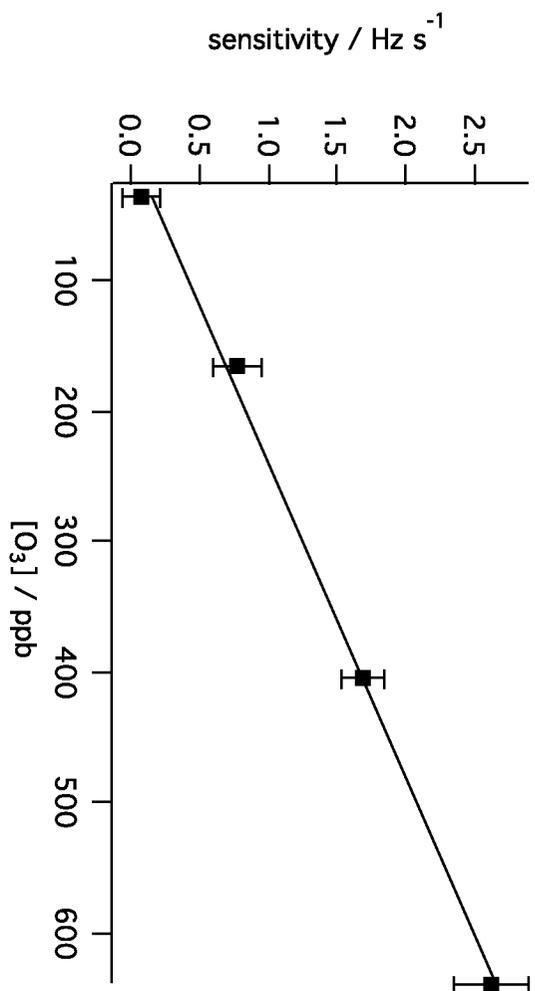
Figure 3
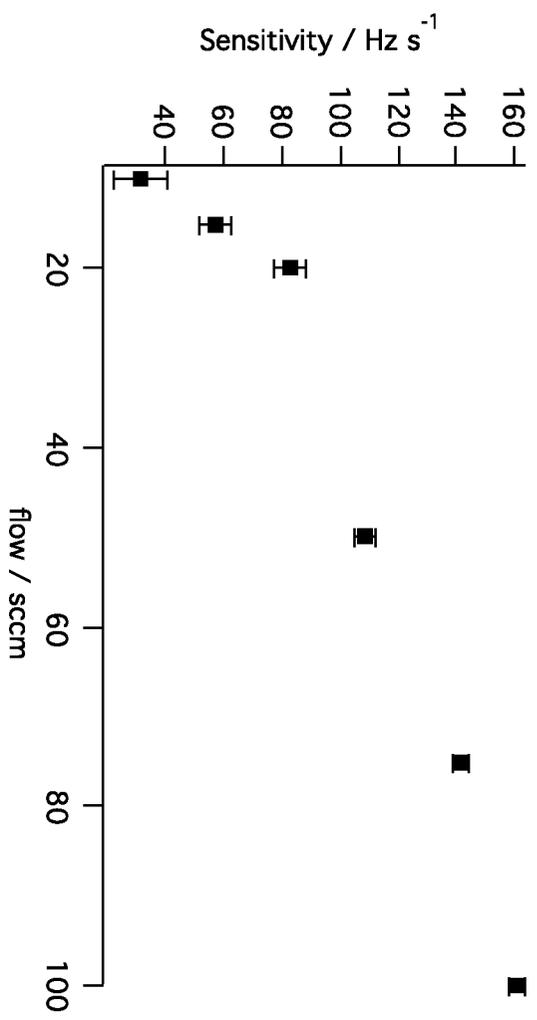
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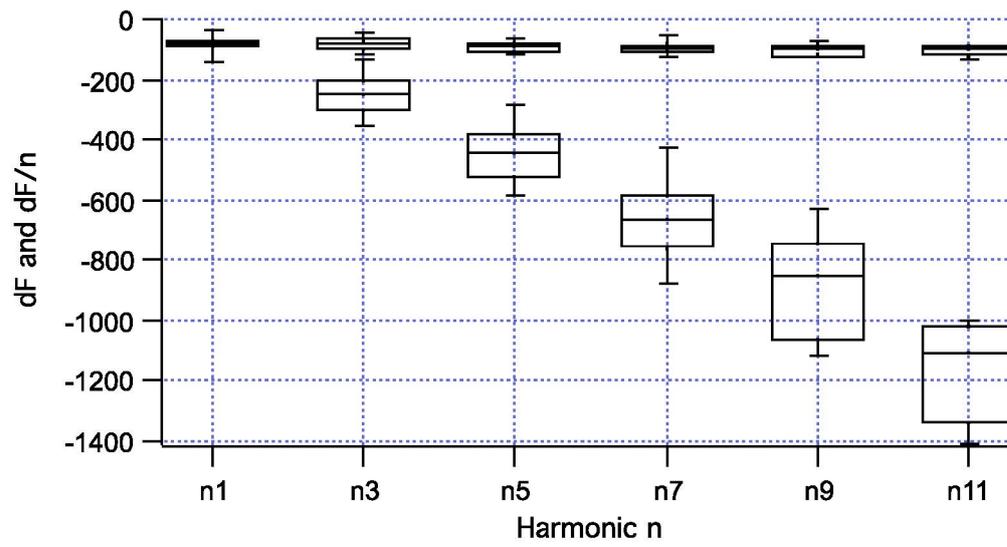
Short Summary

Tropospheric ozone is an important greenhouse gas and thus influences climate but it is also secondary air pollutant relevant to air quality. Therefore, understanding the budget of ozone is of crucial importance as it can significantly alter the oxidative capacity of the atmosphere on regional and global scales. New ozone detection techniques are being continuously developed. The development of low cost sensors could potentially provide both high sensitivity and fast response devices to measure ozone. In this work a coated acoustic wave sensor has been developed to selectively detect atmospheric ozone. A coated quartz crystal microbalance was used for ozone detection. The following different reactive coatings for ozone sensing were tested: beeswax, gallic acid, indigo carmine, polybutadiene, potassium iodide and sodium nitrite. Polybutadiene was found to have the highest sensitivity with respect to ozone. This novel work shows that ozone detection can be improved by operating at the crystals' harmonic frequencies and in conjunction with a suitable flow rate, a potentially highly sensitive and fast response sensor can be created based on acoustic wave technology.

Graphical abstract