

USE OF SODIUM TETRACHLOROMERCURIATE AS A SUBSTRATE
FOR THE DETERMINATION OF SO₂ ON THE
PIEZOCRYSTAL DETECTOR

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ABSTRACT

An experimental glass-tight piezoelectric crystal cell has been developed for studying gas-solid reactions on piezoelectric quartz crystals and several substrates have been evaluated for the determination of SO₂ in ambient air. Sodium tetrachloromercuriate adsorbs from 0.18 to 4.01 µg of SO₂ in 15 minutes periods and shows the best results. A study of the effect of the voltage and temperature applied to the piezoelectric crystal has also been performed.

INTRODUCTION

Piezoelectric quartz crystals are currently used for frequency control in communications equipment, selective filters in electrical equipment, measurement of the temperature and the dew point of gases, and in very accurate clocks. King¹ demonstrated that quartz crystals could also be used as sorption detectors by coating the crystals with appropriate compounds. In these applications advantage is taken of the very high sensitivities of the vibrating crystal to the adsorption of materials on the crystal surface.

The presence of a solid on the crystal surface will alter the frequency of vibration, but the amplitude is hardly affected. A film of liquid or solid on the surface, however, reduces the amplitude of the vibration, and if a gas dissolves into the liquid or solid, the amplitude is reduced further.

The change in frequency of the oscillating quartz crystal according to the Sauerbrey equation²

$$\Delta F = -0.38 \times 10^6 \times \frac{F}{T} \times \frac{\Delta W}{A} \quad (1)$$

where ΔF is the frequency change due to the coating, in Hz, F is the frequency of the quartz plate in MHz, A is the area of the coated electrode in cm^2 , T is the thickness of the plate in cm, and ΔW is the weight of the deposited film in grams. For common crystals this equation is reduced to,

$$\Delta F = -2.3 \times 10^6 \times F^2 \times \frac{\Delta W}{A} \quad (2)$$

This equation predicts that commercially available 15 MHz crystal having electrodes 5 mm in diameter will have a mass sensitivity of 2600 Hz per μg of material absorbed by the crystal. A detection limit of about 10^{-12} g can be calculated indicating the piezoelectric crystal detector to possess the potential of being one of the most sensitive of all detectors.

Some of the substrate coatings that have been used include liquids such as squalane or silicone oil for the detection of hydrocarbons, polar liquids such as sulfolane to detect polar organic compounds, solid such as silica gel or alumina for the measurement of water vapor, metal films and salts, such as silver, copper or lead acetate for the detection of hydrogen sulfide.¹

Olin³ developed a piezoelectric aerosol particle mass concentration monitor for the determination of the actual mass concentration of an aerosol cloud.

Bond⁴ used piezoelectric quartz crystals to study the sorption of a series of chloresteryl esters and recently, Guilbault, Lopez-Roman and Billedeau⁵

studied the reactions of mono-, di-, and tri-methylamine with some transition metals salts by using piezoelectric crystals on a vacuum line. Guilbault⁶ used mercuric bromide as a coating for the piezoelectric crystal detector and studied the reaction with diisopropylmethyl phosphonate. Hartigan⁷ used piezoelectric devices for amine classification and for SO₂ detection.

The analysis of SO₂ in air have been a problem for about 60 years since Hahn⁸ developed the first technique which was based on the ability of SO₂ to discharge the color of iodine-starch solutions. Bassett and David⁹ reported the reaction between the iodine-iodide system for its determination of SO₂ and Martin and Grant¹⁰ developed a galvanic coulometric monitoring system for the determination of sulfur dioxide in air. Using gas chromatography, Obermiller and Charlier¹¹ pointed out the inability of the thermal conductivity detector to detect SO₂ at ambient concentrations. The flame ionization detector, on the other hand, fails to respond at all to permanent gases. Recently, Ziebriski¹² developed a method for the determination of SO₂ by using an argon ionization detector with a radioactive ⁶³Ni source and found a detection limit of 50 ppm of SO₂, limit too insensitive to directly measure air pollutants in typical air concentrations.

The present report is concerned about the use of the well known West-Gaeke¹³ reaction for the determination of sulfur dioxide in air samples by coating the piezoelectric crystal with sodium tetrachloromercuriate and also by using some gas chromatographic liquid phases.

EXPERIMENTAL

Apparatus and Reagents

A new all glass gas-tight piezoelectric crystal cell has been designed and constructed specially for this project. Figure 1 shows the geometry of the glass piezoelectric crystal cell, with a Swagelok 1/4" union with a septum in the inlet and a 1/4" cup in the outlet. Two Wolfram-Nickel leads supplied

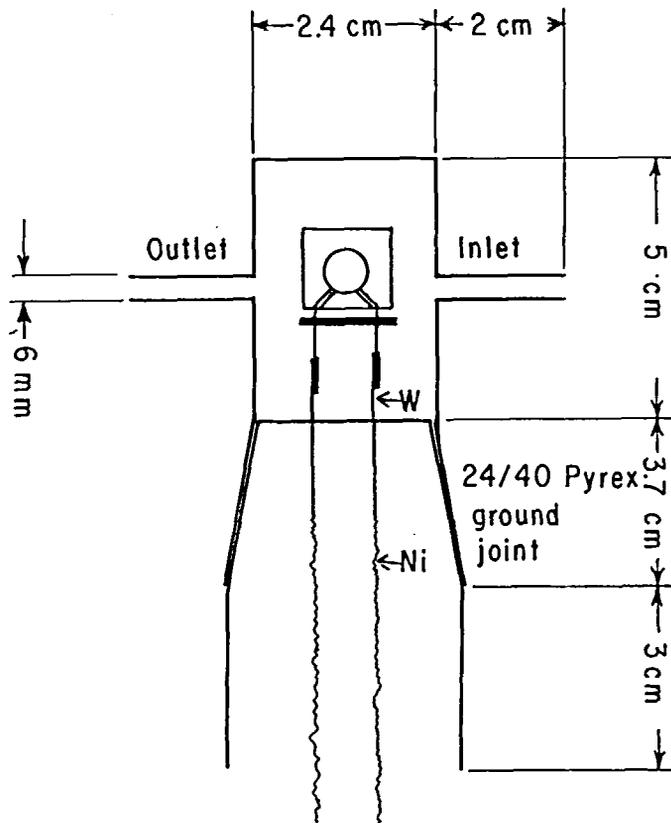


FIGURE 1

Glass Piezoelectric Crystal Cell

by Union City Weld Corporation were introduced into the glass cell base with 1/4" long pieces of stainless steel hypodermic needles (No. 18) soldered to the above wires to provide an easy way to connect the pins of the piezoelectric crystal to the oscillator.

The oscillator used contained three turning sockets built with an OX transistor oscillator low frequency kit (6 to 10 MHz) supplied by International Crystal, Oklahoma. The pins of the crystal were connected to the oscillator by a 2 ft. long wire and the oscillator was connected to a Heath 1-30 VDC

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solid state regulator power supply model IP-28. The frequency meter was a Systron Donner Frequency/period Meter Model 8050. This counter has a range of 0-30 MHz with a resolution of 0.1 Hz and an accuracy of ± 1 count. It was capable of displacing a maximum of any five consecutive digits to the left and automatically positioning the decimal point.

The crystals used in these studies were 9 MHz quartz crystals with a plated metal electrode (7.9 mm diameter), AT cut in a HC 6 U holder supplied by Piezoelectric Crystal Co., Carlisle, Pennsylvania.

Reagents

Sodium tetrachloromercuriate 0.1 M, was prepared by mixing 2.7 g HgCl₂ supplied by Matheson and with 1.11 g of NaCl supplied by Baker and adding water to 100 ml.

Sulfur dioxide was from a Matheson lecture cylinder.

Apiezon N, silicone SE-30, Silicone QF-1, carbowax QF-1, carbowax 20 M and versamid 900 were supplied by Analabs and 1% solutions in chloroform were prepared except for the versamid 900 that was dissolved in hot chloroform-butanol 1:1.

RESULTS AND DISCUSSION

The first experiments were performed to determine the effect of crystal coating on the frequency of the crystal. King¹⁴ reported that the method used for coating was not critical provided that resulting coating was smooth. Since Sauerbrey's equation was derived for smooth thin-films it would follow that a rough substrate surface would not have the weight-sensitivity predicted by the equation. Attempts to achieve a smooth coating on the crystal were made by dipping the crystal into a solution of the coating material, then letting the water dry at 110°C in an oven for 15 minutes. This technique was not satisfactory due to a lack of reproducibility and smoothness.

The most satisfactory technique for coating crystals was to spray the substrate with a Spray Kit supplied by Pierce Chemical Co. Since the most sensitive part of the crystal is the electrode, a piece of a plastic film with an 8 mm diameter hole was placed on the crystal during spraying. This technique provided a smooth coating and about $\pm 2 \mu\text{g}$ of substrate can be applied to the crystal by spraying the 1% solution during about 5 seconds at 12 cm of distance.

An experiment was performed to determine the effect of the voltage applied to the oscillator. When the voltage applied to the oscillator increased from 4 to 9 volts the frequency increased about 150 cycles. On the other hand the frequency of the 14 MHz crystal decreased about 500 cycles when the voltage applied to the oscillator increased from 4 to 9 volts. Results are shown in Figures 2 and 3. According to these experiments 5.5 volts was chosen to be applied to the oscillator in order to vibrate the 9 MHz crystals.

A study was performed to determine the effect of temperature on the frequency of a clean or coated crystal. The cleaned or coated crystal was placed inside the oven of a Hewlett-Packard Gas Chromatograph Model 5750 B and temperatures from 25 to 200°C were applied to the crystals. The crystals were coated with a 1% solution of apiezon N in chloroform. The results are shown in Figures 4 and 5 for the 9 MHz crystals. In both cases the frequency of the crystals increased with increases in temperature, especially from 100° to 200°C. From 25° to 40°C the effect of the temperature is very small, an increase of about 40 cycles. Therefore, these experiments show that temperature must remain constant during the reading; but a change of 10°C is not critical.

In order to achieve a piezoelectric crystal detector specific for SO₂, several substrates have been tried in a static system and evaluated as coatings for the determination of SO₂. Among them are, sodium tetrachloromercurate, apiezon N, silicone SE-30, silicone QF-1, carbowax

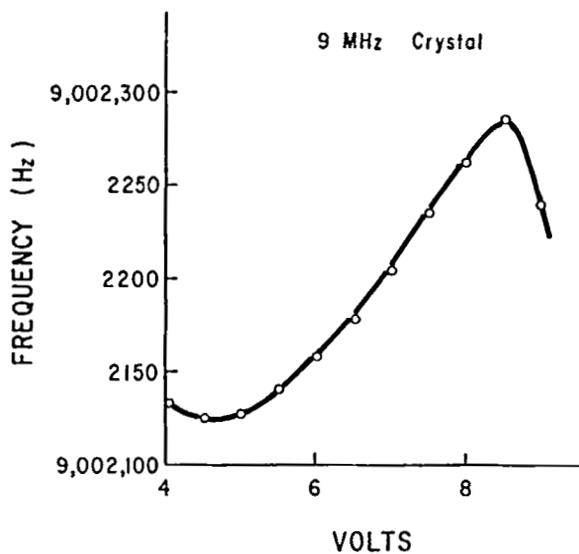


FIGURE 2

Effect of Voltage Applied to a 9 MHz Crystal

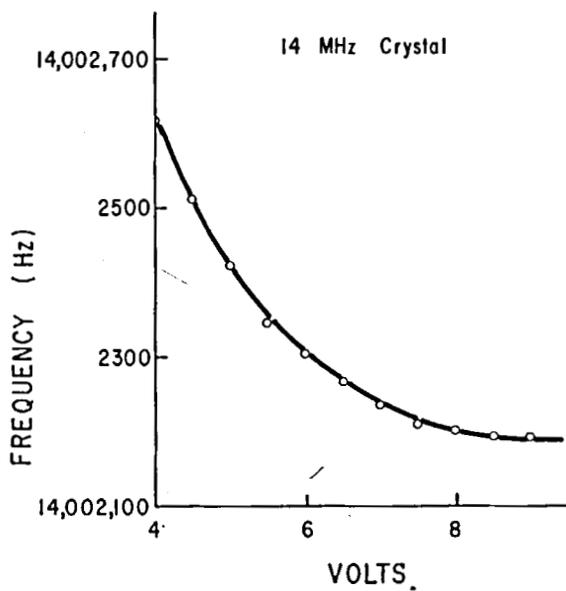


FIGURE 3

Effect of Voltage Applied to a 14 MHz Crystal

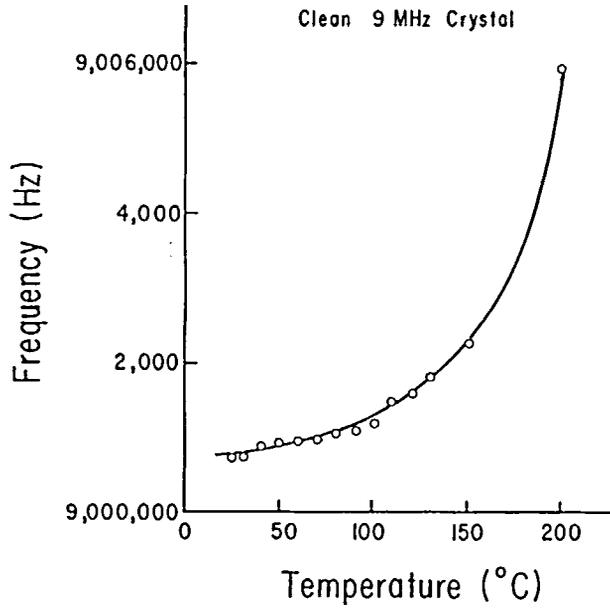


FIGURE 4

Effect of Temperature on the Frequency of a Clean 9 MHz Crystal

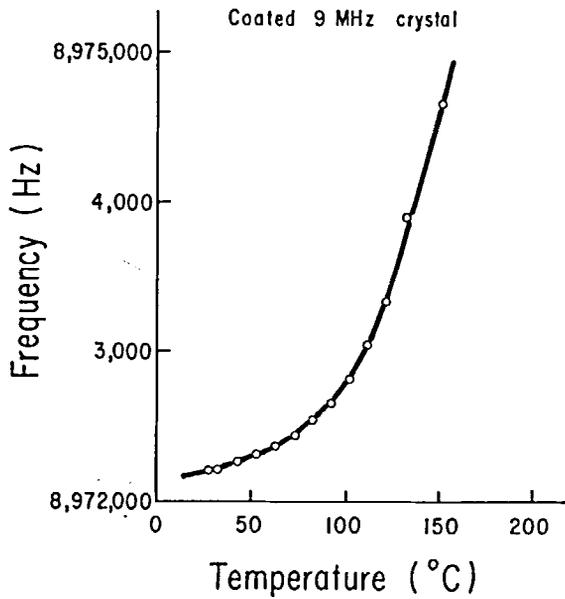


FIGURE 5

Effect of Temperature on the Frequency of a Coated 9 MHz Crystal

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20M and versamid 900. The concentration of the coating was in all cases 1% in chloroform except for the tetrachloromercurate that was 0.1M. These solutions were sprayed on the electrode of the crystal and after drying in an oven at 110°C for ten minutes, the crystal was placed on the piezoelectric crystal cell to evaluate each substrate. Fifty µl of SO₂ was injected in the cell with a 100 µl gas tight Hamilton syringe. The µg of SO₂ adsorbed by the coating were calculated according to the Sauerbrey equation [2]. From 13.612 to 16.325 µg of each substrate was applied to the crystal and readings were taken from 10 seconds to 15 minutes as illustrated on Table 1. Sensitivity of the 9 MHz crystal was calculated to be 369 Hz/µg.

Results are summarized on Table 1 where it is possible to conclude that the best coating for the determination of SO₂ is sodium tetrachloromercuriate. A study of the linearity of the coated crystal with tetrachloromercuriate was made. All frequency readings were taken after one minute

TABLE 1

Time (minutes)	Blank (no coating)	µg. of SO ₂ adsorbed using the coating					
		[HgCl ₄] ²⁻	apiezon N	Silicone SE-30	Silicone QF-1	Carbowax 20 M	Versamid 900
0.10	-	0.181	0.126	0.082	0.070	0.030	0.063
0.20	-	0.390	0.148	0.089	0.088	0.041	0.125
0.30	-	0.612	0.172	0.097	0.122	0.082	0.142
1	-	0.805	0.182	0.097	0.149	0.102	0.195
2	-	1.101	0.188	0.103	0.168	0.113	0.208
3	0.004	1.433	0.210	0.111	0.265	0.118	0.231
4	0.021	2.051	0.235	0.114	0.284	0.151	0.252
5	0.048	2.322	0.281	0.141	0.330	0.162	0.301
10	0.075	2.980	0.298	0.149	0.350	0.184	0.352
15	0.081	4.011	0.340	0.194	0.404	0.201	0.381

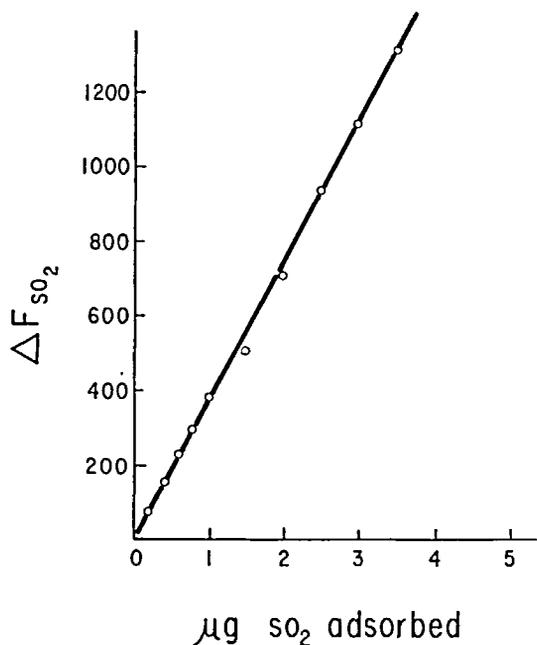


FIGURE 6

Sorption of SO_2 on sodium tetrachloromercuriate
Frequency Change of a 9MHz Crystal

and results are represented in Figure 6. From this study it is possible to conclude that sodium tetrachloromercuriate will adsorb SO_2 , and from 0.18 to 4.01 μg can be detected in a 15 minute period. Therefore this coating can be used for the determination of SO_2 in ambient air.

Results using other coatings for the determination of SO_2 , NO , NO_2 , H_2S and NH_3 will be published later. Gas chromatographic detectors specific and sensitive for these air pollutants are being currently developed.

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