

LA-UR- 97 - 1789

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Title: MEASURING GAS COMPOSITION AND PRESSURE  
WITHIN SEALED CONTAINERS USING ACOUSTIC  
RESONANCE SPECTROSCOPY

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Submitted to: CONFERENCE PROCEEDINGS  
NINTH INTERNATIONAL CONFERENCE ON HIGH  
TEMPERATURE MATERIALS CHEMISTRY  
MAY 19-23, 1997  
PENN STATE

RECEIVED  
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## MEASURING GAS COMPOSITION AND PRESSURE WITHIN SEALED CONTAINERS USING ACOUSTIC RESONANCE SPECTROSCOPY

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Interim and long-term storage of carefully prepared plutonium material within hermetically sealed containers may generate dangerous gas pressures and compositions. We have been investigating the application of acoustic resonance spectroscopy to non-intrusively monitor changes in these parameters within sealed containers. In this approach a drum-like gas cavity is formed within the storage container which is excited using a piezoelectric transducer mounted on the outside of the container. The frequency response spectrum contains a series of peaks whose positions and widths are determined by the composition of the gas and the geometry of the cylindrical resonator; the intensities are related to the gas pressure. Comparing observed gas frequencies with theory gives excellent agreement. Small changes in gas composition, better than 1:1000, are readily measurable.

### INTRODUCTION

The interim storage of plutonium containing materials has raised concerns about the generation of dangerous gas pressures and gas compositions in the hermetically sealed containers. Pure plutonium oxide powders, if not properly prepared, can generate pressures exceeding 700 psi of H<sub>2</sub>.(1) Noninvasive characterization techniques would allow storage containers to be monitored for changes in gas composition and gas pressure. Being able to monitor containers will help to ensure the long-term safety of the materials stored under DOE's repackaging program.

Gas-filled acoustical resonators have been used for monitoring gas composition and to make routine accurate measurements of the speed of sound in gases.(2),(3) The accuracy of acoustic techniques can be extraordinary; the universal gas constant R has been determined with an uncertainty that is a factor of five smaller than the uncertainty using other techniques.(4)

We have been investigating the application of acoustic resonance spectroscopy for monitoring changes in the gas pressure and gas composition in sealed storage containers. The goal of this work is to design a robust, economical characterization system that can be used on containers destined for interim storage.

## EXPERIMENTAL

In order to observe resonant gas modes a resonant cavity must exist within the storage container that is accessible to ultrasonic transducers mounted on the outside of the container. The resonant cavity must be of a simple geometry for which the wave modes can be confidently modeled. The cylindrical geometry of the container itself could be used. Radial gas modes can be excited in the head space above the material in the container. This approach works fine for an empty container; however when small amounts of an energy absorbing material such as silica sand (surrogate for plutonium dioxide) are added the energy of the gas mode is damped to the point of being undetectable.

We have fashioned a cylindrical, drum-like gas cavity within the storage container from a section of pipe with ends parallel fastened onto the bottom of a storage can with a circular plate glued on top as a lid. The circular plate has a 50 micron filter fitted onto a small hole in order to let gas pass into the cavity while keeping out the material in the can. The storage container is filled with silica sand. This experimental geometry is shown in Fig. 1. The sand effectively dampens all modes associated with the container except those from the area on the bottom of the can that is protected by the cavity. Transducers are glued to the bottom of the can.

Spectra are acquired using a Neel Electronics Portable Digital Synthesizer and Analyzer Model DSA300. This unit sends a sine wave variable in amplitude from 0-10 V peak-to-peak to an x10 amplifier and then to the excitation transducer. Signal from a pick-up transducer is amplified and fed back to the DSA300. This signal is mixed with two sine waves having phases 90 degrees apart, low pass filtered, and amplitude measured. The result is the real and imaginary components of the signal which are converted by the data acquisition program to the amplitude and phase of the signal. The frequency of the sine wave is swept to produce a spectrum.

## RESULTS

### Resonant Frequencies

The formula for the resonant frequency of a gas-filled cylindrical cavity is well known from classical acoustic theory.(5) The general solution for the cylindrical case is

$$v = \frac{c}{2} \sqrt{\left(\frac{n_z}{l}\right)^2 + \left(\frac{\alpha_{n,m}}{a}\right)^2} \quad [1]$$

where  $l$  is the height of the cylinder,  $a$  is the radius,  $c$  is the velocity of sound of the gas,  $n_z$  is the index for the longitudinal waves and takes on the values of 0, 1, 2, 3..., and  $\alpha_{n,m}$  is the index of the radius where the derivative of the integer Bessel function is zero. The values of  $\alpha_{n,m}$  given in Table I.(6)

Table 1. Values for  $\alpha_{n,m}$ .

m\n	0	1	2	3	4
0	0.0000	1.2197	2.2331	3.2383	4.2411
1	0.5861	1.6970	2.7140	3.7261	4.7312
2	0.9722	2.1346	3.1734	4.1923	5.2036
3	1.3373	2.5513	3.6115	4.6428	5.6624
4	1.6926	2.9547	4.0368	5.0815	6.1103
5	2.0421	3.3486	4.4523	5.5108	6.5494
6	2.3877	3.7353	4.8600	5.9325	6.9811
7	2.7304	4.1165	5.2615	6.3477	7.4065
8	3.0709	4.4931	5.6576	6.7574	7.8264

Spectra were acquired with the container under vacuum and with the container filled with argon at a pressure of 40 psia. Comparison of the two spectra allowed the identification of thirty three of a possible fifty gas mode resonances over the frequency range of 0 - 12,900 Hz. All resonances that appeared in the spectrum of the pressurized container were matched with calculated resonances. The gas resonances were typically 20 Hz FWHM and the amplitudes of the stronger resonances were typically one tenth the amplitude of the background. The frequency of the observed gas mode resonances was estimated from the spectra and fit to Eq. 1 by varying the height and radius of the cylinder. This procedure yielded  $l = 3.833$  cm and  $a = 8.544$  cm with a standard deviation of the differences of 8 Hz.

### Amplitude

The amplitude of a gas mode resonance is a function of the gas pressure, the gas composition, and the presence of a container mode. The amplitude of resonances due to helium are substantially smaller than the amplitude of resonances due to argon. The amplitude of gas mode resonances that occur at the same frequency as strong container resonances can be larger by several orders of magnitude than the amplitude of gas mode

resonances that occur at frequencies where there is only a small background signal. This effect can be observed by gradually shifting a gas mode toward a container resonance by changing the gas composition. Nevertheless, the amplitude of gas mode resonances can be used to obtain pressure information. The amplitude of a gas resonance peak not appreciably affected by container resonances increases linearly with gas pressure. The amplitude of an argon gas mode as a function of pressure is shown in Fig. 2. At pressures lower than about 10 psia the amplitude deviates from the straight line behavior observed at higher pressures.

### Fitting the Observed Spectra

The observed spectra must be fit using an appropriate lineshape function to obtain quantitative information concerning the amplitude, frequency, and linewidth. We shall use  $\nu$  (Hz) for the frequency instead of the circular frequency  $\omega$  (rad sec<sup>-1</sup>) because the data is obtained in terms of Hz. Resonance motion corresponds to the solution for the forced motion of a damped harmonic oscillator. The lineshape function is given by

$$response(\nu) = \frac{\frac{\nu_0}{\tau}}{\left[ (\nu_0^2 - \nu^2)^2 + \left( \frac{\nu}{\tau} \right)^2 \right]^{0.5}} \quad [2]$$

where  $\nu$  is the driving frequency which is swept to obtain the spectrum,  $\nu_0$  is the center frequency,  $\tau$  is related to the linewidth by  $FWHM \cong \frac{\sqrt{3}}{\tau}$ , and the numerator  $\frac{\nu_0}{\tau}$  normalizes the function to one at  $\nu = \nu_0$ . The phase varies as the driving frequency passes through the center frequency and is given by

$$\phi = \tan^{-1} \left( \frac{\nu / \tau}{\nu^2 - \nu_0^2} \right) \quad [3]$$

where  $\phi$  is the angle by which the displacement leads the driving force. These functions are illustrated in Fig. 3.

The observed signal is the amplitude of a sine wave that results from summing the sine wave contributions from the gas mode resonance and any background signal. The background signal arises from the sum at the observed frequency of all container resonances. In general there is a phase difference in the sine waves due to the gas mode resonance and the background signal which gives rise to asymmetric line shapes. The observed signal may go up if the phase difference is close to zero or it may go down if the phase difference is close to  $\pi$ . The observed signal is fit to a model with parameters for a

linear background amplitude, the gas mode amplitude, the gas mode linewidth, and the phase difference between the background and the gas mode. The nonlinear least squares fitting routine uses Levenberg-Marquadt minimization. *Atypical* fit is shown in Fig. 4.

### The Effective Mass

Information concerning the gas composition is obtained from the velocity of sound. The observed gas resonance frequency,  $\nu$ , and dimensions of the cylindrical cavity are used to calculate the velocity of sound of the gas using Eq. 1. The velocity of sound is related to the average mass of the gas and the heat capacity ratio  $\gamma$  by,

$$c^2 = \frac{\gamma \cdot RT}{\langle M \rangle} = \frac{\langle C_p \rangle}{\langle C_v \rangle} \cdot \frac{RT}{\langle M \rangle} \quad [4]$$

where  $\langle \rangle$  signifies the ensemble average. For a gas mixture containing only monatomic gases  $\gamma$  is 5/3. An effective mass,  $M_{\text{eff}}$ , can be defined for any gas as

$$\langle M_{\text{eff}} \rangle = \frac{\langle M \rangle}{(1 - \delta)} \quad [5]$$

where  $\delta$  is a correction factor that arises because the heat capacities of polyatomic gases are different from those of an ideal monatomic gas. The value of  $\delta$  ranges between 0 (monatomic gases) and 0.3. The effective mass is calculated directly from the observed frequency once the geometry and temperature are known. The effective mass and gas mode resonant frequencies for a number of common gases are given in Table 2 using the geometry shown in Fig. 1. The spread of frequencies are illustrated in Fig. 5.

Table 2. The heat capacity at room temperature, mass, effective mass, speed of sound, and gas mode frequency of some common gases.

Gas	Cp J/mol K T=293.15	Cp/R T=293.15	Cp/Cv T=293.15	$\delta$	M (g/mol)	$M_{\text{eff}}$	c (m/s)	Frequency (Hz)
H <sub>2</sub>	28.8009	3.4640	1.4058	0.1565	2.0159	2.3899	1310.41	9036
N <sub>2</sub>	29.1213	3.5025	1.3996	0.1602	28.0134	33.3588	350.74	2418
O <sub>2</sub>	29.3517	3.5302	1.3952	0.1629	31.9988	38.2242	327.66	2259
CO	29.1420	3.5050	1.3992	0.1605	28.0104	33.3647	350.71	2418
CO <sub>2</sub>	36.8804	4.4357	1.2911	0.2254	44.0098	56.8135	268.76	1853
H <sub>2</sub> O	33.5738	4.0380	1.3292	0.2025	18.0153	22.5898	426.23	2939
He	20.7860	2.5000	1.6667	0.0000	4.0026	4.0026	1012.57	6982
Ne	20.7860	2.5000	1.6667	0.0000	20.1830	20.1830	450.92	3109
Ar	20.7860	2.5000	1.6667	0.0000	39.9480	39.9480	320.52	2210



## CONCLUSIONS

Predictable resonant gas modes can be observed in a storage container filled with powder and fitted with an appropriate resonant cavity. Line positions reflect changes in gas composition and amplitudes are proportional to changes in gas pressure. Well established theory relates geometry, speed of sound, and frequency. Observed spectra, even when complicated by interaction with strong container modes, can be fit to obtain quantitative information on line positions, amplitudes, and line widths. Comparing observed frequencies with frequencies calculated from our geometry, temperature, and known gas composition gives excellent agreement. Our data indicate that small changes in gas composition, better than 1:1000, will be readily measurable. An effective molar mass, a combination of the mean molar mass and the mean heat capacity ratio, can be calculated for unknown gas mixtures from the speed of sound computed from the observed gas resonances.

## ACKNOWLEDGEMENTS

Funding for this effort was made possible through the Nuclear Materials Stabilization Task Group, EM-66 of the Department of Energy. Los Alamos National Laboratory is operated by the University of California for the United States Department of Energy under contract W-7405-ENG-36.

## FIGURES

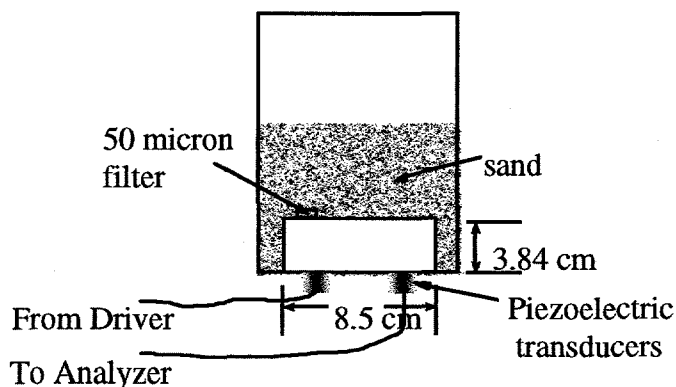


Fig. 1. Schematic of a storage can with a cylindrical cavity. Acoustic resonance spectra are acquired by driving a piezoelectric transducer glued to the bottom of the container with a variable frequency sine wave and picking up the response of the system using a second transducer.

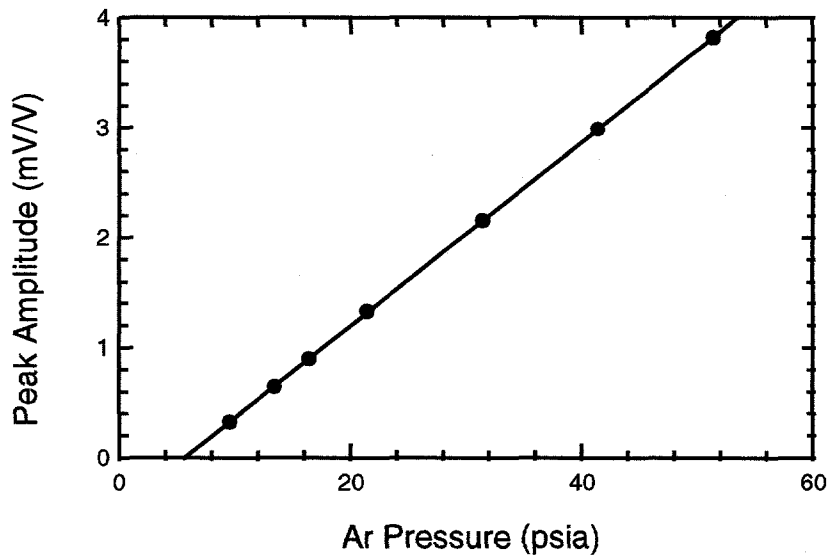


Fig. 2. The amplitude of an argon gas resonance from a cylindrical cavity as a function of argon gas pressure. The gas resonance was chosen to be far from container resonances. The response at pressures lower than 10 psia deviate from the straight line shown here.

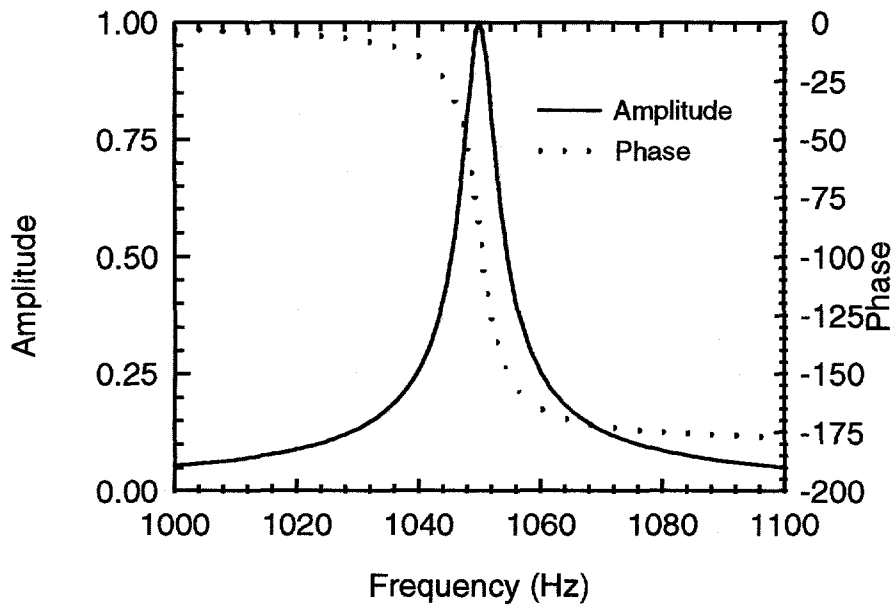


Fig. 3. The amplitude and phase of a forced harmonic oscillator using Eqs. 2 and 3.

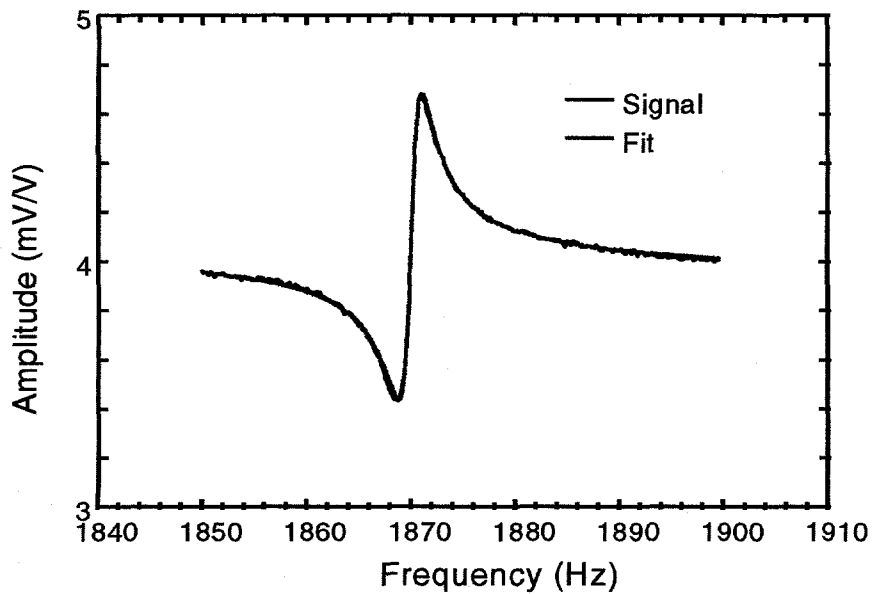


Fig. 4. A typical fit to a gas mode resonance of argon using the lineshape and phase of a forced harmonic oscillator as described by Eqs. 2 and 3. The gas mode resonance is nearly  $-\pi$  out of phase with the background signal resulting in the amplitude initially decreasing as the resonance is approached.

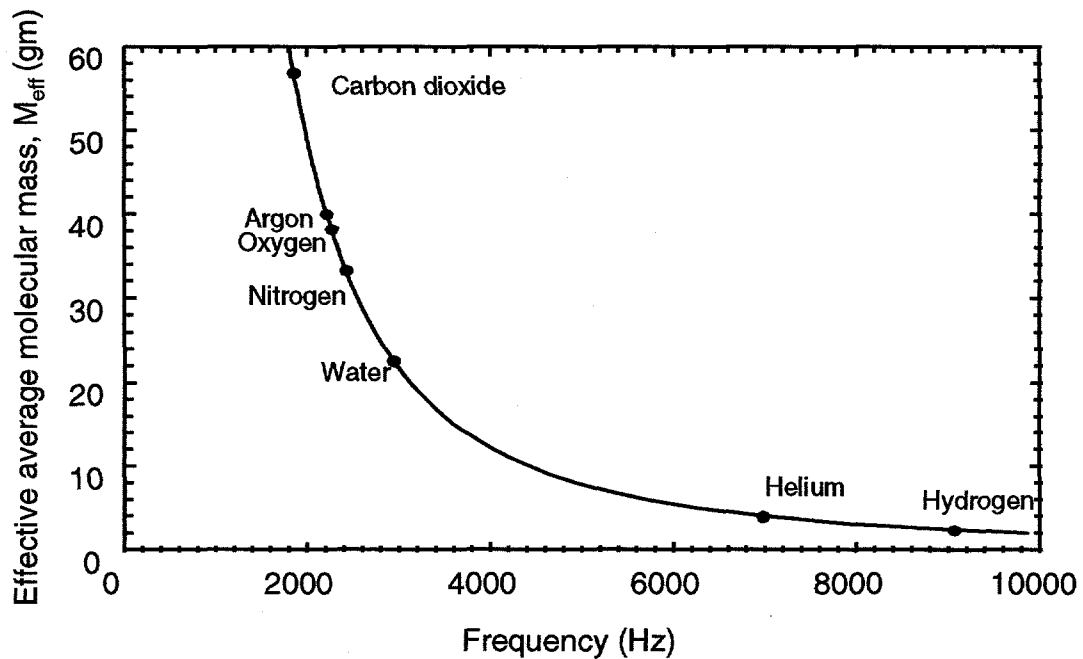


Fig. 5. The effective mass can be obtained directly from the observed frequency. The frequencies for a cylindrical cavity of dimensions shown in Fig. 1 result in the effective mass shown here. The positions for some common gases are shown for illustration.

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