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FEASIBILITY DEMONSTRATION FOR HYDROGEN CHLORIDE DETECTION USING A CHEMISORPTION TECHNIQUE AND A QUARTZ CRYSTAL MICROBALANCE

By David W. Jex and Gary L. Workman Space Sciences Laboratory

December 1975



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16. ABSTRACT

A method of measuring concentrations of hydrogen chloride between 1 part per billion and 10 parts per million at standard temperature and pressure is presented.

The feasibility of a low-cost device incorporating a chemisorption technique coupled with a quartz crystal microbalance was demonstrated in the field at the Viking B launch using a Titan-Centaur vehicle from Kennedy Space Center on August 20, 1975. Hydrogen chloride is a product of solid rocket combustion. The concentration level of hydrogen chloride for this particular launch was measured as approximately 0.2 parts per million at 4 km from the launch site.

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TECHNICAL MEMORANDUM X-64984

FEASIBILITY DEMONSTRATION FOR HYDROGEN CHLORIDE DETECTION USING A CHEMISORPTION TECHNIQUE AND A QUARTZ CRYSTAL MICROBALANCE

I. INTRODUCTION

There is a growing awareness and concern about the atmospheric pollutant gases that are being distributed in our environment. One of the gases of concern is hydrogen chloride (HCl), which is extremely hydroscopic. The concerns range from the effects gaseous and/or aqueous concentrations may have on individual health to the effects of reactions that contribute to the depletion of the ozono layer.

A letter from the National Research Council expresses the limits to which an individual may be exposed as 8 parts per million (ppm) and further states:

"The STPL's (Short-term Public Limits) for HCl were established by the committee on Toxicology in August 1971. They are:

10 minutes at 4 ppm

- 30 minutes at 2 ppm
- 60 minutes at 2 ppm
- 1 hour daily at 2 ppm

5 hours/day, 3 to 4 days/month at 0.7 ppm

The other PEL's (Public Emergency Limits) for HCl are: 30 minutes at 20 ppm 60 minutes at 10 ppm."

Therefore, it is necessary that suspected high concentrations or repeated exposures to HCl in the troposphere be measured to insure personal safety.

Another concern is expressed by Dr. Fred Kaufman, a chemical kineticist at the University of Pittsburgh, and his research group who are studying the reactions involving HCl which lead to the depletion of the ozone layer, such as the sequence,

 $HCl + OH \rightarrow H_2O + Cl$ $Cl + O_3 \rightarrow ClO + O_2$

These reactions result in a net loss of ozone molecules which may contribute to depletion of the ozone layer.

While many methods and instruments are available to measure the concentration of HCl, most of them are expensive, cumbersome, and delicate. An inexpensive, portable, and rugged device which can be refurbished easily and remotely operated would be extremely valuable. Such a device has been conceived and its feasibility demonstrated. The device combines chemisorption techniques with a quartz crystal microbalance. The theory, application, and demonstration of this device are discussed in the remainder of this report. The device is called a CATCH (continuous accumulation and time correlated history) detector.

II. THEORY

Basically, we must establish a theoretical model and relationship between the measurement parameters and the gas we desire to monitor. To accomplish this we will initially summarize the Maxwell-Boltzmann law in classical statistical thermodynamics, adapting it to the microbalance measurements of HCl. It will be noted that chemisorption is assumed here to be time independent.

The molecular model employed is based on the following six classical assumptions:¹

1. ANY MACROSCOPIC VOLUME OF A GAS CONTAINS A VERY LARGE NUMBER OF MOLECULES. This assumption is justified by all experimental evidence. The number of molecules in a kilomole (Avogardro's number N_A) is

 6.03×10^{26} ... At standard conditions, 1 kilomole of an ideal gas occupies 22.4 m³. Hence at standard conditions there are approximately 3×10^{25} molecules in a cubic meter, 3×10^{19} in a cubic centimeter, and 3×10^{16} in a cubic millimeter.

2. THE MOLECULES ARE SEPARATED BY DISTANCES THAT ARE LARGE COMPARED WITH THEIR OWN DIMENSIONS AND ARE IN A STATE OF CONTINUOUS MOTION. The

^{1.} Francis W. Sears and Gerhard L. Salinger: Thermodynamics, Kinetic Theory, and Statistical Thermodynamics, Third Edition, Copyright 1975, Addison-Wesley Publishing Company, Reading, Massachusetts, pp. 251-252.

diameter of a molecule, considered as a sphere, is about 2 or 3×10^{-10} m. If we imagine one molal volume at standard conditions to be divided into cubical cells with one molecule per cell, the volume of each cell is 30×10^{-27} m³. The length of one side of such a cell is about 3×10^{-9} m, which means that the distance between molecules is of this order of magnitude, about 10 times the molecular diameter.

- 3. TO A FIRST APPROXIMATION, WE ASSUME THAT MOLECULES EXERT NO FORCES ON ONE ANOTHER EXCEPT WHEN THEY COLLIDE. Therefore between collisions with other molecules or with the walls of the container, and in the absence of external forces, they move in straight lines.
- 4. COLLISIONS OF MOLECULES WITH ONE ANOTHER AND WITH THE WALLS ARE PERFECTLY ELASTIC. The walls of a container can be considered perfectly smooth, so that there is no change in tangential velocity in a collision with the walls.
- 5. IN THE ABSENCE OF EXTERNAL FORCES, THE MOLE-CULES ARE DISTRIBUTED UNIFORMLY THROUGHOUT THE CONTAINER. If N represents the total number of molecules in a container of volume V, the average number of molecules per unit volume, n, is

$$n = N/V$$

The assumption of uniform distribution then implies that in any element of volume ΔV , wherever located, the number of molecules ΔN is

$$\Delta N = n\Delta V$$

Obviously, the equation above is not correct if ΔV is too small, since the number of molecules N, although large, is finite, and one can certainly imagine a volume element

so small that it contains no molecules, in contradiction to the equation above. However, it is possible to divide a container into volume elements large enough so that the number of molecules per unit volume within them does not differ appreciably from the average, and at the same time small enough compared with the dimensions of physical apparatus that they can be treated as infinitesimal in the mathematical sense and the methods of differential and integral calculus can be applied to them. For example, a cube 1/1000 mm on a side is certainly small in comparison with the volume of most laboratory apparatus, yet at standard conditions it contains approximately 30 million molecules.

6. THE DIRECTIONS OF MOLECULAR VELOCITIES ARE ASSUMED TO BE DISTRIBUTED UNIFORMLY. To put this assumption in analytic form, imagine that there is attached to each molecule a vector representing the magnitude and direction of its velocity. Let us transfer all these vectors to a common origin and construct a sphere or arbitrary radius r with center at the origin. The velocity vectors, prolonged if necessary, intersect the surface of the sphere in as many points as there are molecules and the assumption of uniform distribution in direction means that these points are distributed uniformly over the surface of the sphere. The average number of these points per unit is

 $\frac{N}{4\pi r^2}$

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and the number in any element of area ΔA is

$$\Delta N = \frac{N}{4\pi r^2} \Delta A$$

wherever the element is located. As in the preceding paragraph, the area must be large enough (that is, it must include a large enough range of directions) so that the surface density of points within it does not differ appreciably from the average. Because of the large number of molecules, the range of directions can be made very small and still include a large number of points.

Using polar coordinates $(\mathbf{r}, \theta, \phi)$, the number density of molecules with velocities having directions between θ and $\theta + \Delta \theta$, and ϕ and $\phi + \Delta \phi$ is

$$\Delta n_{0\phi} = \frac{n}{4\pi} \sin \theta \, \Delta \theta \, \Delta \phi \qquad (1)$$

Not all molecules will have the same speed, but rather will have speeds that range from zero to infinity.

It is assumed that in an equilibrium condition the number of molecules with velocity in any specified range will remain constant; i.e., although a given molecule may lose or gain speed and change direction due to a collision with another molecule and/or a surface, some other molecule in the system is also changing its velocity so that the distribution of velocities remains constant.

The molecular flux (Φ) at any surface is defined as the total number of molecules arriving (ΔN) at the defined area (ΔA) per unit time (Δt); hence,

$$\Phi = \frac{\Delta N}{\Delta A \Delta t} \qquad (2)$$

The construction of an arbitrary plane surface in space and the development of an equation for the molecules that will be incident on that surface results in the classical formula for the flux:

$$\Phi = 1/4 \,\mathrm{n}\,\overline{\mathrm{v}} \tag{3}$$

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where n is the number of molecules/m³, and \bar{v} is the average velocity of the molecules in m/s. The flux Φ is then the number of molecules/m²/s.

Using the Maxwell-Boltzman speed distribution function

$$\Delta \boldsymbol{\mathscr{H}}_{v} = \frac{4N}{\sqrt{\pi}} \left(\frac{m}{2kT}\right)^{3/2} v^{2} \exp\left(-\frac{m}{2kT}\right) \Delta v \qquad , \qquad (4)$$

the definition of the average or arithmetic mean speed

$$\bar{\mathbf{v}} = \frac{1}{N} \sum \mathbf{v} \Delta \boldsymbol{\mathcal{M}}_{\mathbf{v}}$$

and approximating the sum by an integral we get

$$\bar{\mathbf{v}} = \left(\frac{8\mathrm{kT}}{\pi\,\mathrm{m}}\right)^{\frac{1}{2}} \qquad . \tag{5}$$

The ideal gas law gives us

PV = NkT or $\frac{N}{V} = \frac{P}{kT} = n$ (6)

Then by substituting equation (5) into equation (3), we obtain the Maxwell-Boltzmann flux which can be expressed in terms of the number of molecules/m³ (n), the temperature (T) in K, the mass (m) in kg, and Boltzmann's constant $(k) = 1.3806 \times 10^{-23} \text{ J/K};$

$$\Phi = 1/4 n \bar{v} = 1/4 n \left(\frac{8}{\pi} \frac{kT}{m}\right)^{1/2} \qquad .$$
 (7)

In equation (6), the number of molecules/ m^3 can be expressed in terms of the pressure (P) in N/m², Boltzmann's constant (k), and the temperature (T) in K. Theoretically, it can be calculated from equation (6) that the number of molecules/ m^3 at standard temperature (273 K) and pressure (1.0132 × 10⁵ N/m²) is:

$$n = \frac{P}{kT} = 2.7 \times 10^{25} \text{ molecules/m}^3 \text{ or } 2.7 \times 10^{19} \text{ molecules/cm}^3$$

For air quality measurements, we need to relate parts per million or billion, the accepted terms for air quality discussion, to molecules/cubic centimeter. Therefore, if we assume that there is 1 ppb $(1 \text{ ppb} = 1 \times 10^{-9})$ of atmospheric pollutant gas at standard temperature and pressure (STP), then the number of these molecules (n') will be one billionth the total number of molecules, or

$$n' = \frac{n}{1 \times 10^3} = 2.7 \times 10^{10} \text{ molecules/cm}^3$$

To determine the flux, we must identify the atmospheric pollutant gas so that we may obtain either the average velocity or mass to use in flux equation (7). For the purpose of this report, we will identify HCl. Since HCl is hydroscopic, the probability that the HCl molecule will attach itself to a water molecule must be taken into account. For the sake of simplicity and to be on the conservative side, let us assume that each and every HCl molecule has an H₂O molecule attached to it. The mass (m') of such a combined molecule is 9.04×10^{-26} kg/molecule, and the average velocity, at a temperature of 273° K, calculated from equation (5) would be 325.8 m/s or $325.8 \times 10^{2} \text{ cm/s}$.

Substituting these results into equation (7) to obtain the flux, when the concentration level is 1 ppb, yields

$$\Phi = \frac{1}{4} \text{ n' } \overline{v} = 2.2 \times 10^{14} \text{ molecules/cm}^2/\text{s}$$

Assuming that a surface with a chemisorption coefficient of unity is available for these incident, combination molecules, the rate of accumulation would be

$$\Phi m' = 1.99 \times 10^{-8} \text{ gm/cm}^2/\text{s}$$

This is substantiated by an alternative approach using de Boer's equations which give

$$\Phi m' = (3.52 \times 10^{22}) \frac{p}{(mT)^{1/2}} = 1.9 \times 10^{-8} \text{ gm/cm}^2/\text{s}$$

where $p = (1 \text{ ppb}) 760 \times 10^{-9} \text{ mm}$ of mercury, $T = 298^{\circ}$ K, and m = 54.5 gms.

Therefore, it is possible to measure low concentrations of atmospheric pollutant gases provided the relationship between the sensitivity of the detector and the adherence of the molecules to the surface of the detector is correctly balanced; i.e., if the chemisorption coefficient, defined as the ratio of molecules of interest that adhere to the surface divided by the total number that come in contact with it, is 1 and the sensitivity of the detector is 2×10^{-8} gm/cm²/s, then the concentration of 1 ppb can be measured as discussed. If the chemisorption coefficient is 0.1 and the sensitivity of the detector is 2×10^{-9} gm/cm²/s, the concentration of 1 ppb would again be measurable. Therefore, it is the relationship between the chemisorption coefficient and the sensitivity of the detector the sensitivity of the detector is 2×10^{-9} gm/cm²/s, the concentration of 1 ppb would again be measurable. Therefore, it is the relationship between the chemisorption coefficient and the sensitivity of the detector that determines the measurable concentration.

III. APPLICATION

The detection of an atmospheric pollutant gas like HCl in low concentrations can be accomplished as discussed in the preceding section. The problem is broken into two parts: the sensitivity of the detector and the adherence of the molecules to the detector surface. For this discussion, assume the chemisorption process to be independent of time.

Since there exist a multitude of techniques and microbalances that cover the sensitivity scale down to 10^{-9} gm/cm², this aspect of the problem merely becomes one of selecting the proper means for measuring the range desired. The real-life problems make it a little more difficult than implied in the above statement; however, in practice it is still a process of choice.

The second aspect, developing or devising a method whereby the molecules of interest can be coupled to the measurement surface, remains as a problem to be solved.

For the purpose of this report and for a more detailed discussion, we have identified HCl as a gas of interest and have assumed a concentration level of 1 ppb. Because this is a very small molecule, even with the water molecule attached, it is very lightweight, and a very sensitive microbalance is required.

In this case, let us choose a 10 MHz quartz crystal microbalance whose sensitivity is on the order of 10^{-9} gm/cm²-Hz. The sensitivity of a particular quartz crystal is found by using the formula²

2. A. W. Warner: Micro Weighing with Quartz Crystal Oscillators—Theory and Design, Chapter 5, p. 143.

$$\mathbf{m}^{\prime\prime}/(\mathbf{A}\Delta \mathbf{f}) = (1/\mathbf{f}) \ \rho \ \mathbf{t} \tag{8}$$

where m¹¹ is the mass collected in grams, A is the collecting area in cm², Δf is the change in frequency (Hz), f is the crystal frequency (Hz), ρ is the density of the quartz in gm/cm³, and t is the thickness of the crystal in cm. Assuming $f = 1 \times 10^7$ Hz, $\rho = 2.56$ gm/cm³, and t = 0.016 cm, the sensitivity (s) would be 4.2×10^{-9} gm/cm²/Hz.

To simplify calculations, we will derive a formula for the concentration level (c) as a function of the parameters of the molecules of interest and the quartz crystal microbalance:

$$\mathbf{c} = \frac{\text{number of molecules of interest}}{\text{total number of all molecules}} = \frac{\mathbf{n'}}{\mathbf{n}} = \frac{4\Phi kT}{P\left(\frac{8}{\pi}\frac{kT}{m}\right)^{1/2}}$$
(9)

where

$$\Phi = (\text{molecules/m}^2/\text{s}) = \frac{(\Delta f/\Delta t) \text{s}^{\dagger}}{\text{m}}$$
(10)

and

$$s' = (1 \times 10^{-3} \text{ kg/gm})(1 \times 10^{4} \text{ cm}^{2}/\text{m}^{2})s = 4.2 \times 10^{-8} \text{ kg/m}^{2}/\text{Hz}$$

;

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therefore, substituting equation (10) into equation (9) yields

$$\mathbf{c} = \frac{4(\Delta f/\Delta t) \, \mathrm{s'kT}}{\mathrm{m} \, \mathrm{P}\left(\frac{8 \, \mathrm{kT}}{\pi \, \mathrm{m}}\right)^{1/2}} = \left(\frac{\Delta f \mathrm{s'}}{\Delta t}\right) \left(\frac{1}{\mathrm{m} \, \overline{v}}\right) \, \frac{4\mathrm{kT}}{\mathrm{P}} \tag{11}$$

where Δf is the change in frequency (Hz), Δt is the elapsed time (s), s' is the sensitivity of the quartz crystal (kg/m²/s), k is Boltzmann's constant (J/K), T is the temperature (K), m is the mass of the molecule (kg), P is the pressure (N/m²), and \bar{v} is the average velocity of the molecules (m/s).

With this formula, we can solve for the concentration, assuming that all the molecules of interest, and only these molecules, are adhering to the surface of the quartz crystal. To have confidence in this assumption it is necessary to provide a surface which is selective and which has a known stay time or sticking coefficient.

Athens College, working through contract NASS-28058, recembered that an aromatic amine [triphenylamine $([C_6H_6]_3)$] be used because tertiary amines are less reactive toward water vapor and H_2SO_4 if the substituents (in this case, 3 phenyl groups) are large and nonpolar. The low vapor pressure of large molecular weight amines also increases their usefulness for mass measurements with the quartz crystal microbalance.

The successful technique for bonding this amine to the surface of the quartz crystal was to vapor deposit the triphenylamine on the crystal surface in a vacuum chamber. The amount of triphenylamine can be monitored during this process, and reproducible coatings are possible. Since the boiling point of triphenylamine is approximately 365°C, the coated CATCH detector is durable to the high temperature limit of the quartz crystal microbalance.

Several quartz crystals of the sensitivity described earlier $(4.2 \times 10^{-9} \text{ gm/cm}^2/\text{s})$ were coated with the amine and exposed to HCl and other mixtures and substances. While these preliminary tests were not calibrated, they did show the selective nature and some of the characteristics between the amine, HCl, and the quartz crystal microbalance.

At this point, a chance to demonstrate the feasibility of such a device in the field by measuring HCl as a by-product of solid rocket propellant combustion during Viking launches from Kennedy Space Center was provided through the efforts of Dr. Briscoe Stephens. He originally stimulated the investigation into the possible application of such a device in the measurement of HCl while he was working with the Joint MSFC-LaRC-KSC (Marshall Space Flight Center-Langley Research Center-Kennedy Space Center) Rocket Exhaust Effluent Diffusion Prediction and Monitoring Team. Because the Viking launches from KSC represented the last potential opportunity to field test this ''new'' technique in conjunction with other supporting instruments under actual launch conditions, further calibration was postponed. However, it is recognized that the chemisorption coefficients and parameters are needed together with a more detailed analysis of the pollutant gas reaction characteristics.

IV. DEMONSTRATION

The opportunity to demonstrate feasibility of the CATCH detector was provided at the Viking B launch from Cape Kennedy on August 20, 1975. It

occurred before the calibration of the instrument could be completed. However, since it represented the last opportunity to field test this new technique, five crystals were coated and dispersed at three locations around the launch site. Only one of these three locations, with two operating detectors, was on a line from the launch site over which a portion of the exhaust cloud passes at a height of several hundred meters. This location was 4 km from the launch site, and the data recorded are presented in Figure 1.

Several facts are necessary to interpret the results:

1. Data points are 3 minutes apart due to the time-sharing sequence of the recording instrumentation.

2. Data points are the average of 44 frequency readings taken during a 1-minute interval. The standard deviation (σ) is 50 Hz.

3. An increasing frequency indicates a decrease in the temperature.

4. A decreasing frequency indicates an increase in the thickness or mass addition to the crystal. Therefore, detection of HCl is a negative-going peak.

5. The two detectors were at different heights above ground level. Detector A was 4 m (13 ft) above the ground and detector C was 1.8 m (6 ft) above the ground.

Keeping these facts in mind, the data in Figure 1 indicate an abrupt change in the temperature of detector C about 5:35 p.m. A similar, but smaller, shift occurs in detector A. Unfortunately, the temperature at this location was not monitored; therefore, a quantitative verification cannot be made. However, a severe thunderstorm moved in from the southwest and blocked out the sun, causing an abrupt, physically noticeable change in the temperature as noted by the operator during this time period. During the other time periods the rate of increase in frequency is regular, which would be indicative of a slowly changing temperature.

Between 5:40 and 5:50 p.m. both detectors record a negative-going peak of the same amplitude (~150 Hz). Both peaks occur during the time the exhaust cloud was seen visibly to pass overhead as recorded in the log book by the operator. The lowest portion of the visible exhaust cloud was several hundred meters above the ground. The amplitude of the peaks is 3σ and, therefore, from statistics represents less than a 5 percent probability of being a random deviation. For these reasons, it is concluded that these events represent a measurement of HCl with a rise time of 180 s. Using these values in

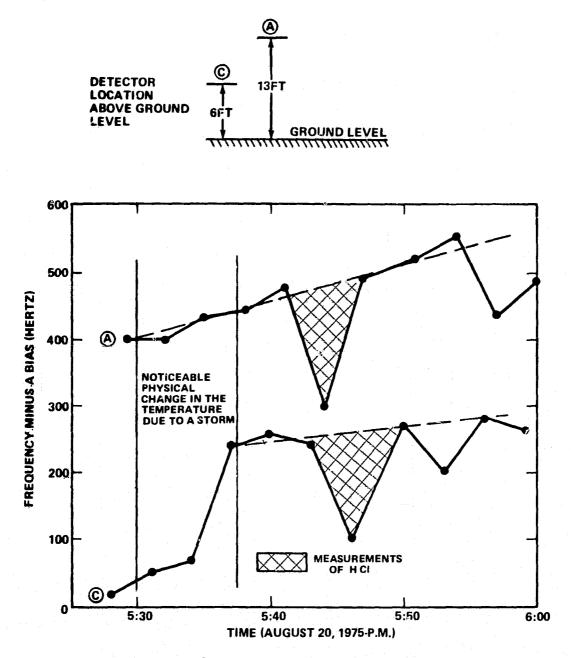


Figure 1. Plot of data obtained from modified quartz crystal microbalances (2 each) located at station P-2.

equation (11) for the concentration level, the calculated concentration (C_c) at STP is 0.2 ppb.

Preliminary laboratory experiments indicate that the ratio of incident molecules to the number that are chemisorbed is not unity. Assuming a low value of 0.001, as suggested by the laboratory experiments, for the chemisorption. ratio (α) gives

 $C = \frac{1}{\alpha} C_c = 200 \text{ ppb or } 0.2 \text{ ppm}$.

The data also show smaller negative peaks later which are not designated as HCl measurements. While it is possible that they are HCl indicators, either they are not detected by both CATCH detectors at the same time or their amplitude is less than 2σ . Therefore, they are left unexplained.

It can be seen from Figure 1 that the capture and measurement process was followed by a loss of the HCl molecules. This phenomenon is in contradiction to the premise of chemisorption upon which the theory is based. The laboratory tests indicate that this effect is real and consistent with measurements of HCl in the atmosphere using this technique. Investigations are presently being pursued to establish the basis for the phenomenon and why it does not follow the theorized chemisorption process.

V. CONCLUSION

There is a growing awareness and concern for atmospheric pollutant gases which are being distributed in our environment. HCl, one of these gases, causes concerns which range from the effect gaseous and/or aqueous concentrations may have on individual health to the effect of reactions that contribute to the depletion of the ozone layer.

It is, therefore, important that an HCl monitoring system be proposed and demonstrated that would be small, low cost, portable, and remotely operable. These features would provide a means of measuring concentrations of HCl in locations that vary from the open troposphere to the freshman chemistry laboratory.

A device which meets these criteria has been described and discussed in this document. It couples a chemisorption technique with a real-time, mass-

monitoring quartz crystal microbalance. The quartz crystal microbalance is sensitive to approximately 10^{-9} gm (10^{13} molecules of HCl) and is, therefore, capable of measuring concentrations of HCl down to 1 ppb at STP. The feasibility of this device was demonstrated at the Viking B launch at Cape Kennedy on August 20, 1975, where HCl was a by-product of the solid propellant combustion. The data from this test indicated a concentration level of 0.2 ppm at 4 km from the launch site based on a chemisorption coefficient of 0.001.

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APPROVAL

FEASIBILITY DEMONSTRATION FOR HYDROGEN CHLCRIDE DETECTION USING A CHEMISORPTION TECHNIQUE AND A QUARTZ CRYSTAL MICROBALANCE

By David W. Jex and Gary L. Workman

The information in this report has been reviewed for security classification. Review of any information concerning Department of Defense or Atomic Energy Commission programs has been made by the MSFC Security Classification Officer. This report, in its entirety, has been determined to be unclassified.

This document has also been reviewed and approved for technical accuracy.

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