

# INCORRECT ASSUMPTION OF BORON TRIFLUORIDE HYDROLYZATION TO HYDROGEN FLUORIDE AND THE EFFECT ON EXISTING MONITORING TECHNIQUES

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## Abstract

Recently, the reliability of leak detection techniques for boron trifluoride gas,  $\text{BF}_3$ , has been called into question. Typically, boron trifluoride is monitored indirectly as hydrogen fluoride, HF, based on the assumption that  $\text{BF}_3$  instantly hydrolyzes to form HF upon contact with humid air. An understanding of the chemical reaction of anhydrous  $\text{BF}_3$  stored in gas cylinders and the environment into which it leaks is fundamental to any environmental health and safety program seeking to monitor it. This paper provides background to the assumption of hydrolyzation, the current question of sensor reliability, and a thorough examination of the chemical reaction. The discussion shows conclusively that HF is not formed as a result of  $\text{BF}_3$  exposure to moist air. The paper then discusses how this information affects four current gas monitoring techniques: Fourier Transform Infrared (FTIR) spectrometer; Molecular Emission Spectrometer (MES) or flame ionization; Mineral Acids Chemcassette<sup>®</sup> (1) tapes; and electrochemical cells. It is demonstrated that only the latter method is incapable of adequately monitoring  $\text{BF}_3$  due to its inherent reliance on the assumption of  $\text{BF}_3$  hydrolyzation to HF.

## INTRODUCTION

Of the many hazardous materials used in the semiconductor manufacturing process, boron trifluoride gas,  $\text{BF}_3$ , is currently one topic of debate. In 1992, the Sunnyvale, California Fire Department began to question why sensor testing was being performed using materials other than  $\text{BF}_3$  (2). Subsequently, GasTech, Inc., of Newark, California, a gas sensor manufacturer, issued a letter recalling their electrochemical  $\text{BF}_3$  sensors. The letter stated that actual sensor response tests performed with  $\text{BF}_3$  gas showed the sensors to be unreliable and unable to monitor the gas around the required Threshold Limit Value (TLV) of 0-1 part per million (ppm) (3).

To ensure worker safety and to minimize loss of production, reliable gas detection systems are necessary to detect leaks and automatically shut down the gas flow. There are primarily four types of sensing technologies used in the industry today. The Fourier Transform Infrared (FTIR) spectrometer is a device that measures the concentration of a predetermined airborne compound by reading its interaction with an infrared beam. The Molecular Emission Spectrometer (MES) or flame ionization is similar to the FTIR in that an analyzer monitors the energy emitted from the ionized gas after it passes through a hydrogen flame. Electrochemical cells are frequently used and measure gas

concentration as the change in conductivity within a cell caused by the reaction of the gas and an electrolyte. Mineral Acids Chemcassette<sup>®</sup> tapes employ a paper tape that is continually passed by a gas source and an optical reader. Any target gas present will stain the tape and then be read by the optic device.

Fundamental to each of these leak detection systems is the actual behavior of the target gas under operating conditions. Recently, there has been some debate over the effectiveness of some of these detection methods for boron trifluoride gas. In order to determine the effectiveness of a monitoring technique, a thorough knowledge of the gas, its effects of exposure to humans, and its behavior under operating conditions must first be gained.

## HISTORY, EFFECTS OF EXPOSURE AND USES OF $\text{BF}_3$

Boron Trifluoride,  $\text{BF}_3$ , one of the four boron trihalide compounds, was first prepared by Gay-Lussac and Thenard in 1809 by the reaction of boric acid and fluorspar at dull red heat (Gay-Lussac and Thenard, 1809). In its anhydrous state,  $\text{BF}_3$  is a colorless, toxic gas with a sharp pungent odor. When exposed to moisture, it undergoes a violent exothermic reaction and forms dense white fumes (Handbook of Compressed Gases, 1990); (4). These fumes

are highly corrosive. Human exposure to boron trifluoride is consistent with that of exposure to fluorboric acid,  $\text{HBF}_4$ . Irritation to the nose, eyes, skin, and respiratory track increase with exposure time and concentration. Although listed as primarily a pulmonary irritant, exposure has been shown to cause dental fluorosis, damage to the liver and kidneys, hypocalcemia (low levels of calcium in the blood), pneumonitis, and death. The Threshold Limit Value (TLV) is listed as 1 part per million (ppm) and no chronic effects have been observed in workers frequently exposed to low levels over a period of several years. However, an exposure of 50 ppm for 30-60 minutes may be fatal (Matheson Gas Data Handbook, 1980); (4).

Boron trifluoride is used as a Lewis acid catalyst in many different operations including isomerization, alkylation, polymerization, nitration, and halogenation, and also in Friedel-Crafts reactions for the synthesis of saturated hydrocarbons (Kroschwitz and Howe-Grant, 1995); (4). More pertinent to this paper is its use as a dopant in the semiconductor manufacturing process.

## DISCUSSION

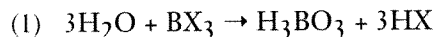
### CURRENT PROBLEM

The most common  $\text{BF}_3$  gas leak detection methods are the electrochemical sensors and the chemcassette tape readers. Both of these systems were designed around the assumption that  $\text{BF}_3$  behaves as other similar halides and hydrolyzes upon contact with ambient moisture. Many of the halide-containing process gases, such as boron trichloride,  $\text{BCl}_3$ , hydrogen chloride,  $\text{HCl}$ , dichlorosilane,  $\text{H}_2\text{SiCl}_2$ , phosphorous oxychloride,  $\text{POCl}_3$ , and tetrachlorosilane,  $\text{SiCl}_4$ , are monitored as the hydrolyzed hydrogen halide ( $\text{HCl}$  or  $\text{HF}$ ). Under this assumption,  $\text{BF}_3$  hydrolyzes instantly to form hydrofluoric acid,  $\text{HF}$ . An electrochemical cell monitoring device measures the concentration of  $\text{HF}$  in the airstream by the change in conductivity of the electrolyte between two electrodes. Therefore, an increase in millivolt (mV) output is proportional to an increase in the  $\text{HF}$  concentration. This  $\text{HF}$  concentration is assumed to correlate with the actual concentration of  $\text{BF}_3$ . The same is true for the chemcassette tape. A sampling tube draws air from the airstream and any  $\text{HF}$  present stains the tape, the color and intensity of which is a function of the concentration. The stain is then scanned by the optical reader and displayed as a ppm concentration of  $\text{HF}$ . However, this assumption of hydrolysis was never questioned in the development and installation of  $\text{BF}_3$  sensors. Before proceeding further, this assumption must be investigated and the behavior of the gas under operating conditions must be determined.

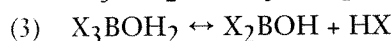
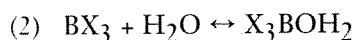
### BEHAVIOR OF $\text{BF}_3$ GAS WHEN EXPOSED TO AMBIENT AIR

It has been widely published that boron trihalides undergo a protonolysis of the boron-halogen bond when contacted

with hydrogen ions. For example, the overall reaction with water is shown as follows, where X represents fluorine, chlorine, bromine, or iodine (Muetterties, 1967):

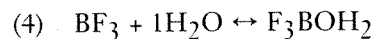


This overall reaction is the foundation on which electrochemical cell and chemcassette tape devices were designed to monitor boron trihalide process gas leaks. Because of the speed at which the end products are reached, equation (1) is generally accepted as the reaction, disregarding the intermediate steps. However, by examining the intermediate reactions, a greater understanding of the hydrolyzation process can be gained. The halides follow an addition and elimination reaction as follows:

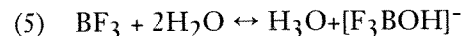


Equation (2) and (3) are very fast for the electrophilic boranes such as the halides or diborane,  $\text{B}_2\text{H}_6$ , with the notable exception of  $\text{BF}_3$ . In that case, equation (2) is fast, but the  $\text{F}_3\text{BOH}_2$  which is formed is quite stable, and therefore prevents the protonolyses from proceeding to completion (Muetterties, 1967); (Kroschwitz and Howe-Grant, 1995); (4). In fact, only with fluoride can the intermediate reactions and complexes be isolated. A detailed explanation of these intermediate steps will provide insight to the idiosyncrasies of the boron trifluoride and water reaction.

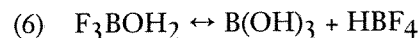
Exposure of anhydrous  $\text{BF}_3$  to even low humidity air results in a rapid exothermic reaction and the formation of dense white fumes. The rate of this reaction is on the order of microseconds and the fumes are aerosol sized droplets of hydrated  $\text{BF}_3$ . Concentrations as low as 1 ppm are known to form these dense white clouds of hydrate. The hydrates are composed of 1/2, 1, 2, or 3 water molecules, depending on the amount of moisture present, bonded to one molecule of  $\text{BF}_3$  (4). By far the most common hydrate to form is the monohydrate of  $\text{BF}_3$ , shown below, which follows equation (2) as expected:



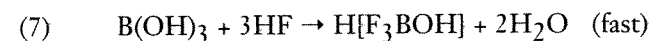
The monohydrate product,  $\text{F}_3\text{BOH}_2$ , is also shown as  $\text{H}[\text{F}_3\text{BOH}]$  or trifluoroboric acid. Other hydrates, such as dihydrate, have been determined by x-ray studies but occur much less frequently (Adams, 1964):

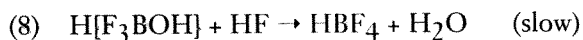


The trifluoroboric acid,  $\text{H}[\text{F}_3\text{BOH}]$ , can be thought of as a boron atom,  $\text{B}^+$ , with three fluoride ligands,  $\text{F}^-$ , and one  $\text{OH}^-$  ligand. In the presence of excess water, the  $\text{F}^-$  ligands are replaced with  $\text{OH}^-$  in a slow dissociation to form boric acid,  $\text{B}(\text{OH})_3$  and fluorboric acid,  $\text{HBF}_4$ .



Any  $\text{HF}$  that forms is quickly scavenged according to the following reactions (Adams 1964); (Sharpe, 1992):





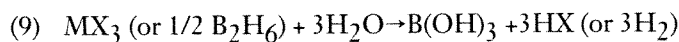
These reactions indicate the ultimate end products of  $\text{BF}_3$  and water to be fluoroboric and boric acid with no hydrofluoric acid at all. In fact, absorption of  $\text{BF}_3$  in water has been performed in glass hardware during controlled experiments. Test results showed the ultimate products to be  $\text{HBF}_4$  and  $\text{B}(\text{OH})_3$ . The fact that no etching of the glass occurred serves as practical evidence that no  $\text{HF}$  or free  $\text{F}^-$  ions were present (Wamser, 1951); (4).

An explanation of why the reaction stops temporarily with the production of  $\text{H}[\text{F}_3\text{BOH}]$ , the monohydrate, is necessary to show that  $\text{HF}$  is not produced. The reason for this fluoride exception to the rule can, in part, be explained by a general discussion of bond energies and thermodynamic stability. Available thermochemical data have produced the following table of calculated bond energies and provide insight to the possible ligand and atom substitutions (Muetterties, 1967):

<b>Bond</b>	<b>Bond Energy (kcal)</b>	<b>Reference Species</b>
BO	188	BO
	164 AV.	$\text{B}_2\text{O}_3$
	133 AV.	$\text{B}(\text{OH})_3$
BF	154 AV.	$\text{BF}_3$
BN	140 AV.	ESTIMATE ( $\text{C}_2$ )
BCl	106 AV.	$\text{BCl}_3$
BH	91 AV.	$[\text{BH}_3]$
	95 AV.	$\text{B}_2\text{H}_6$
BC	82	$\text{B}(\text{CH}_3)_3, \text{B}(\text{C}_2\text{H}_5)_3$
BB	65.5	$\text{B}_2$

Table 1 - Bond Energies

Also helpful is a consideration of the equilibrium constants for the vapor phase hydrolysis of the boron trihalides and diborane in the following reaction (Muetterties, 1967):



<b>Species</b>	<b>Equilibrium constant, K (298°K)</b>
$\text{BF}_3$	$K=10^9$
$\text{BCl}_3$	$K=10^{33}$
$\text{BBr}_3, \text{BI}_3$	$K > 10^{33}$
$\text{B}_2\text{H}_6$	$K=10^{141}$

Table 2 - Equilibria Data

The reactivity of these boranes is dependent on the acceptor strength of the borane and the ease of ligand substitution. The bond energy data suggest that for fluoride, a greater

activation energy is required for equation (2) to proceed past the production of  $\text{X}_3\text{BOH}_2$  (trifluoroboric acid in this case) and achieve  $\text{BF}_3$  hydrolysis. The B-O bond energy is comparable to that of B-F and further suggests greater stability of  $\text{F}_3\text{BOH}_2$  than the other halide forms. Again note that this is also another form of the monohydrate,  $\text{H}[\text{F}_3\text{BOH}]$ . In fact, the intermediate species of  $\text{X}_3\text{BOH}_2$  have not been isolated for the other halides and diborane (Muetterties, 1967). Furthermore, when fluoride is substituted into equation (9), the products are in fact the reactants for the fast reaction of equation (7), which produces  $\text{H}[\text{F}_3\text{BOH}]$ .

While a review of the bond energies and equilibria data only suggest trends and possibilities, a study of the physical structure of the compounds would be more conclusive. The structure of the boron trihalides have been found to be trigonal planar with the individual bond length increasing, as expected, with the size of the halide atom. However, a comparison between the observed bond length, the simple sum of covalent bond radii, and the bond length as calculated using the electronegativity correction of the Schomaker-Stevenson equation all showed significant differences (Muetterties, 1967). Another inconsistency is the fact that a consideration of the electronegativities of the halogens suggests the acceptor strength decreases from trifluoride to triiodide. Yet, in reality, the Lewis acidity of the trihalides (a measure of acceptor strength) places boron trifluoride as the weakest acceptor of the trihalides. These two apparent anomalies may be explained by the hypothesis of a "partial double bond character" resulting from the "back coordination" of an electron pair from the halogen atom to the boron atom (Muetterties, 1967). In fact, the B-F bond is only 28% ionic (Kroschwitz and Howe-Grant, 1995).

Given the structure of the  $\text{BX}_3$  molecule, only three of the four valence shell orbitals of the boron atom are necessary for bonding with the halogen atoms, leaving the remaining  $2p$  orbital of the boron empty. A nonbonding pair of electrons from the halogen atom will flow back and interact with the empty  $2p$  orbital of the boron. This action more or less approximates a conventional double bond, thus the name partial double bond. Consider a similar situation of a transition-metal atom, in a low oxidation state, bonding to six ligands. Without back coordination, the total electron distribution on the metal would increase to impossible levels. Back coordination decreases the overall electron transfer, which reduces the buildup of negative charge on the metal atom, strengthens the metal-ligand bond through this partial double bonding action, and results in a far more stable complex (Porterfield, 1993). As for the boron trihalides, the back coordination theory predicts a much more stable compound structure, and thus a weaker Lewis acidity, for fluorine where the nonbonding electron pair in the  $2p$  orbital interact with the vacant  $2p$  orbital on the boron atom. The stability of the molecule decreases with the back coordination of the nonbonding electron pairs of the  $3p$  orbital of chlorine,  $4p$  orbital of bromine, and the  $5p$  orbital

of iodine (Muetterties, 1967). This ranking of Lewis acidity has, in fact, been determined through laboratory experiments. Not only does the concept of back coordination explain the two anomalies mentioned previously, but it also agrees with the experimentally determined reactions, bond energy data, and equilibrium data presented in this paper.

### IMPACT OF NEW EVIDENCE ON DETECTION METHODS

In light of this evidence, it is clear that under ambient conditions, hydrolyzation of  $\text{BF}_3$  to HF does not occur. Since any leak will instantly form the hydrate,  $\text{BF}_3$  monitoring should be designed to detect the hydrate and not HF, or  $\text{BF}_3$ . The FTIR and the MES devices can be calibrated to do just that, but the other technologies are not as adaptable. As mentioned previously, GasTech, Inc. recalled all their  $\text{BF}_3$  electrochemical sensors as a result of laboratory tests using target gases. The results indicated that sensor response to  $\text{BF}_3$  was "erratic and unrepeatable in magnitude" and therefore the sensors were unable to monitor the target gas to levels around the TLV of 0-1 ppm (3). Results of actual device sensitivity tests showed that other halides such as boron trichloride,  $\text{BCl}_3$ , hydrogen chloride, HCl, dichlorosilane,  $\text{H}_2\text{SiCl}_2$ , phosphorous oxychloride,  $\text{POCl}_3$ , and tetrachlorosilane,  $\text{SiCl}_4$ , produced mV/ppm outputs that accurately correlated the halide concentration to the target gas. Tests for  $\text{BF}_3$  were indeterminate even in very close contact to the source (3). The fact that the  $\text{BCl}_3$  concentrations were sensed accurately as HCl is in keeping with the findings of the boron trihalide chemistry presented above.

Sensitivity tests of Mineral Acid Chemcassette tapes were also performed using  $\text{BF}_3$ . One test, which exposed  $\text{BF}_3$  to "bone dry air", was able to read 1 ppm of  $\text{BF}_3$  as 3 ppm of HF (1). If the air had absolutely no moisture in it, the monitored gas was anhydrous  $\text{BF}_3$ . However, if moisture was present, one molecule of water bonded to one molecule of  $\text{BF}_3$  and formed the monohydrate,  $\text{H}[\text{F}_3\text{BOH}_2]$ , and trifluoroboric acid was monitored. Either way, the result was an acidic compound. Given the nature of the mineral acid chemcassette tape, any type of acid will produce a stain that can be monitored. Again, note that any leak under operational conditions will result in trifluoroboric acid droplets. Any  $\text{BF}_3$  monitoring device should be calibrated to detect trifluoroboric acid.

Other tests were conducted which exposed  $\text{BF}_3$  to air having a wide range of humidity levels. In all cases, the chemcassette was able to detect 1 ppm  $\text{BF}_3$  as 3 ppm or greater HF (1). The greatest sensitivity occurred at humidity levels around 40%, but by 60% relative humidity, the sensitivity was dramatically reduced.

As a result of these tests, several important issues are brought to light. The physical characteristics and set up of the gas cabinet and placement of the sensing devices are critical in how effectively a gas leak is detected. Transport of the  $\text{BF}_3$  to the sensor is affected by dilution with the ven-

tilation air through the cabinet, the actual fluid dynamics inside the cabinet, and the chemistry of the reaction itself.

### PHYSICAL PARAMETERS OF THE GAS CABINET

Gas cylinder storage is an important aspect in ensuring worker safety and reducing loss of production. The Toxic Gas Ordinance (TGO) as well as several other codes outline proper methods for storage; one of which is the gas cabinet. The concept of a gas cabinet is to provide a means of containing any gas leak and venting it through special ductwork to the appropriate form of treatment for the specific gas. This venting is usually accomplished by passing 200 cubic feet of air per minute through the cabinet and into the ductwork. This protects the worker breathing zone by diluting the concentration of any leak and quickly removing the gas from the area. Given the shape of items in the cabinet, laminar flow does not exist throughout the cabinet and "dead spots" due to eddies and vortices may exist that can trap leaked gas. Sensors or sampling tubes are often placed in an area with laminar air flow in order to obtain a representative sample and determine target gas concentration in parts of target gas per million parts of air. The result is that the sensors are frequently placed in the entrance to the ductwork where laminar flow does exist but often not in near proximity to the leak source. This can present problems in terms of dilution and gas transport. Consider for example, a neck leak of 20 cubic centimeters per minute ( $\text{cm}^3$ ). This leak is diluted by 200 cubic feet per minute (cfm) of air vented through the cabinet which serves the purpose of evacuating the gas and protecting the worker breathing zone. However, 200 cfm is equal to 5,663,369  $\text{cm}^3$  and a 20  $\text{cm}^3$  leak of 100% pure target gas is diluted to 3.53 ppm by the time it reaches the sensor. Although dilution is accomplished by the time the gas travels to the ductwork, the concentration near the source is considerably higher. In the case of a  $\text{BF}_3$  leak, the highly corrosive hydrate will attack and damage expensive gas cabinet equipment before a warning alarm sounds at 1/2 the TLV, 0.05 ppm, for occupied areas and 1/4 of the Immediately Dangerous to Life or Health (IDLH), 25 ppm, for unoccupied areas. In fact, a 142  $\text{cm}^3$  leak is necessary to reach a 25 ppm concentration at the sensor to sound the alarm. From this example, it is evident that the dilution, while improving worker safety, makes it much more difficult to monitor the gas properly.

Furthermore transport of the gas to the sensor can affect sensitivity. As mentioned previously, sensitivity tests conducted on chemcassette tapes showed a decrease at relative humidity levels above 40% and a marked decrease at levels above 60%. This is quite possibly related to the chemistry of the reaction. At that moisture level, it is possible that the aerosol sized drops of hydrate begin to coalesce to form large drops which adhere to the sampling tube and never reach the tape. Less moisture will produce fewer droplets of corrosive trifluoroboric acid, which attack the equipment in the cabinet, and facilitate the transfer of  $\text{BF}_3$  to the sensor.

## CONCLUSION

In light of these findings, it has been shown that the basic premise for current boron trifluoride process gas detection is invalid. The FTIR and the MES devices can be calibrated to detect  $\text{BF}_3$  leaks as long as they are set to monitor the appropriate compound, trifluoroboric acid, and not HF or  $\text{BF}_3$ . The mineral acid tapes will, by their inherent reactivity with acids, detect a  $\text{BF}_3$  leak, although the results are still displayed in terms of ppm of HF. For these three workable systems, there are several important operational considerations. The most important of these is to ensure cabinet ventilation does not dilute possible leaks to levels below the desired alarm concentration. Similarly, the corrosive effect of a leak on the cabinet equipment should be considered and alarm concentration adjusted accordingly. A high dilution rate and a low alarm concentration can protect both worker and equipment. The transportation of the sample air and target gas from the probable leak source to the sensor is another important consideration. The aerodynamic flow of air through the gas cabinet can create dead spaces and areas of poor ventilation, thereby impeding the transport of the target gas to the sensor. Also, as discussed previously, the relative humidity can be an important factor for gas transport. The ideal level is 40%. Less moisture allows more of the leaking  $\text{BF}_3$  to remain airborne and be transported to the sensor. It also produces a smaller quantity of corrosive droplets. Finally, this paper shows that electrochemical cell devices are incapable of detecting  $\text{BF}_3$ . The formulation of a different electrolyte could possibly produce a workable device in that trifluoroboric acid will change the conductivity of a solution, however, nothing is currently available.

## ABOUT THE AUTHOR

Ransom Jones grew up on a farm in Middle Tennessee and left home to attend the United States Air Force Academy in Colorado Springs, Colorado. After graduating in the Class of 1993 with a Bachelor's of Science in Civil Engineering, he went to work as an engineer in the 70th Civil Engineering Squadron at Brooks Air Force Base in San Antonio, TX. He then was assigned to complete his Master's of Science in Environmental Engineering at California Polytechnic State University, in San Luis Obispo with a subsequent assignment to Hill Air Force Base in Ogden, Utah as an environmental engineer. He and his wife Kimberly presently live in Enid, Oklahoma where he spends every waking moment learning to fly the T-37 jet trainer at Vance Air Force Base. Ransom hopes to spend the next several years in jet aircraft under 500 feet and over 500 knots.

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## FOOTNOTES

1. Zellweger Analytics, Inc. 405 Barclay Boulevard. Lincolnshire, Illinois 60069. Point of contact: Roberta McMahon, (800) 323-2000. Correspondence with MDA Scientific. Drew Deichmann (408) 261-8802. Compilation of letters and exerts from other sources and Technical Note: Chemcassette Detection of  $\text{BF}_3$ , September 1992.
2. Telephone conversation with the Sunnyvale Fire Department. Ben Gikis (408) 730-7179. 09 January 1997.
3. Correspondence with GasTech, Inc, Newark, CA. Compilation of letters and laboratory tests on electrochemical cell sensitivity to target gases. Point of contact: David Van Heurck (510) 794-6201.
4. Correspondence with Allied Signal, sole manufacturer of boron trifluoride in North and South America. Compilation of letters and Material Safety Data Sheet (MSDS), Number 11FBF-0003, Issue date: 24 September 1996. Point of contact: Mikelle Morris, (302) 791-6757.