

半導体材料ガス中微量水分の分光測定法

Spectroscopic Methods for Trace Moisture Detection in Electronic Specialty Gases

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半導体製造プロセスに使用されるガス中の水分は、酸化等により直接、半導体素子の性能を劣化させるのみならず、配管等の腐食を招き粒子汚染も発生させることが知られており、水分の測定および低減制御技術は、半導体素子の性能のばらつきや歩留まりを低減する上できわめて重要である。半導体素子の高性能化および高集積化に伴い、ガス中の水分測定技術は、より高感度だけでなく、製造プロセスの品質管理に適したオンラインモニタリング能力を有することも要求されるようになった。それらの要求に合致するものとして赤外領域の吸光を利用した各種分光法が米国を中心に開発され、実用化されつつある。分光法は、高感度を得られること、リアルタイム測定が可能であること、非破壊方式であること、検出器等反応性ガスとの接触を避けたい部分を非接触化できることから、次代のオンライン水分測定法として期待されている。

そこで、最新のガス中微量水分測定用分光技術である、フーリエ変換赤外分光装置 (FTIR)、半導体レーザー吸光装置 (TDLAS)、キャビティリングダウン分光装置 (CRDS) による半導体材料ガス中水分測定に関して検討を行った。

FTIR は、広範囲の波長領域を測定することができ、且つ各種最適化を行うことにより 10ppb 程度の検出能力を得られるため、もっとも広く使用されている技術である。FTIR によるホスフィン (PH₃) 中水分の測定を検討した。主成分の干渉が少ない波長域の選定、その波長域において感度を得やすい検出器の選定、水分のバックグラウンドを低減するための適格なパージ方法などを採用することで、数十 ppb の水分測定が可能である。精製器の性能確認に対する使用例を合わせて紹介する。

一方、TDLAS は、半導体レーザーから発する赤外光の吸収を測定する分光装置である。一例として Delta F TDLAS を検討した。これはプロセスガスラインの水分モニターとして設計されており、アンモニア中水分測定について評価した。その結果、9ppb の検出下限を得たが、セル内の圧力変動が測定値に影響することが確認された。これはブロードニング効果と言われるセル内圧力の変化に応じてスペクトル幅が変化する現象に起因したものであると思われる。また、少量の窒素の添加が測定値に影響することも確認され、校正時の標準ガスの使用について注意する必要があることがわかった。アンモニアの精製器による水分低減効果を評価した例を合わせて紹介する。

CRDS (Tiger Optics, MTO 1000) は 3 者の中で比較的新しい技術である。試料ガスを充填し高反射率のミラーを設置したキャビティに、半導体レーザーのパルス光を導入すると、キャビティ内を多数回反射した光の一部がミラーより出てくる。その減衰曲線が試料ガス中の測定対象成分量と相関することを利用して、試料ガス中成分を定量する方法である。原理的にはサブ ppb の検出が期待できる高感度測定技術である。金属酸化物の誘電体から成るミラーが耐食性を有するため、強い腐食性を示す臭化水素 (HBr) および塩素 (Cl₂) 中の水分測定を検討したところ、6ヶ月以上の耐久性を示した。同時に ppb レベルの検出能と高い応答性も確認できた。

これら 3 つの技術に共通する点は、正確に水分を定量するためには、水分量を検出下限より低減したバックグラウンドのスペクトルを得て、試料ガスの測定スペクトルよ

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り差し引く必要があることである。さらに適切なデータ解析と校正手順が必要である。

半導体レーザを用いる2つの技術については、水分の吸収がより強く、且つ主成分の干渉が小さい波長領域の光を発振するレーザの開発が、今後の用途の展開のために重要となる。

Measurement and control of trace impurities in the gases used in semiconductor processing is important to minimize process variations and optimize device yield and performance. In this work, Fourier transform infrared (FTIR) spectroscopy, tunable diode laser absorption spectroscopy (TDLAS) and cavity ring-down spectroscopy (CRDS) are investigated for trace moisture detection. FTIR spectroscopy is applicable to a variety of gases because a wide spectral range is available for moisture detection. As an example, measurement of trace moisture at tens ppb in a phosphine gas matrix, is demonstrated. Laser based techniques are potentially more sensitive than FTIR but are limited to narrow spectral ranges. A prototype TDLAS analyzer specifically designed for moisture detection in ammonia shows a detection limit of 9 ppb and a rapid response to changing moisture concentrations. Tests performed on a commercial CRDS analyzer in corrosive gases such as HBr and Cl₂ show that this instrument is also sensitive to low ppb moisture levels and has good corrosion resistance. For all three techniques, appropriate data analysis that accounts for background interferences and spectroscopic artifacts is key to accurate moisture measurement.

1. Introduction

The performance of many semiconductor devices can be seriously affected by the presence of trace impurities such as moisture in the process gases used during manufacture. In silicon CMOS devices, resist pattern failures, resistivity shifts, diode leakage, junction leakage, lifetime degradation, pitting, hazing and deposition rate change have been associated with moisture contamination or with particles formed as a result of moisture induced corrosion of the gas delivery system. In III-V compound semiconductor devices, trace moisture in the Group V hydride gases can result in lattice defects, unintentional doping, non-radiative recombination centers and undesirable oxide formation that affect properties such as photoluminescence. As device dimensions continue to decrease and higher performance structures are developed, the impact of contaminants on their electrical properties increases. Therefore there is a growing demand for more sensitive and reliable analytical instrumentation that can be used for quality control purposes as well as for on-line monitoring of gases supplied to process tools.

Various instrumental and sensor-based techniques for measurement of trace moisture in electronic specialty gases have recently been reviewed¹⁾. Spectroscopic methods that are based on light absorption measurements in the infrared range that typically follow the Beer-Lambert Law²⁾ are widely accepted and also viewed as the most promising candidates for the next generation of real-time trace moisture analyzers. They are nondestructive and only require optical access to the reactive or corrosive

gas. Further, they provide rapid response times, high sensitivity and selectivity and are suitable for on-line monitoring applications. In this work, we discuss and present results on three spectroscopic techniques, namely Fourier transform infrared (FTIR) spectroscopy, tunable diode laser absorption spectroscopy (TDLAS), and cavity ring-down spectroscopy (CRDS) that have been recently investigated at Matheson Tri-Gas for trace moisture detection in corrosive or hydride gases.

2. Operating Principles and Experimental Set-up

2.1 FTIR Spectroscopy

FTIR spectroscopy is the most widely used of the three techniques at present. Infrared radiation, which has been modulated in a Michelson interferometer, is passed through a gas cell containing the sample and then directed to a light sensitive detector. The resulting interferogram, a plot of IR intensity versus path-length difference, is then Fourier transformed to produce an absorbance versus wavenumber IR spectrum. A background spectrum of the dried cell (and bench) is acquired before sample introduction and used as a reference to obtain the final absorbance spectrum. To increase the instrument sensitivity for trace gas analysis, instruments are typically fitted with a long path-length (5-20 m) multipass cell and a highly sensitive liquid nitrogen cooled Hg-Cd-Te or InSb detector. As exposed parts of an FTIR system can be selected for compatibility with reactive gases, FTIR has been used for detection of trace moisture in various gases including HCl, Cl₂ and NH₃^{3,4)}. Recent work has focused on development of a method for quality control of phosphine cylin-

ders and efficiency testing of purifier media for removal of moisture in phosphine.

FTIR measurements were performed on a Nicolet (Madison, WI) Avatar FTIR spectrometer fitted with a liquid N₂ cooled Hg-Cd-Te detector and a 10m path-length White gas cell. The FTIR bench was purged with purified N₂ and was housed within a purge box to minimize background moisture variations. Moisture in PH₃ was measured at 50°C, 107 kPa, and a flow rate of 1 slpm. The experimental set-up is shown in Fig. 1. The FTIR spectrometer was calibrated by addition of humidified nitrogen to purified PH₃ using a Span Pac moisture generator (Kintek, LaMarque, TX) set up with a NIST calibrated permeation tube. The N₂ concentration in the dry PH₃ was kept below 1% by volume. Nicolet Quantpad software was used to quantify the moisture concentration. QuantPad mathematically combines PH₃ and water reference spectra to fit that of the unknown sample using the classical least squares (CLS) method. The concentration of each component is determined by the prominence of each component's features in the sample spectrum. For optimized sensitivity, regions were selected for each component in which the component's peaks were clearly identifiable and in which interferences from other components were minimized.

2.2 Tunable Diode Laser Absorption Spectroscopy

TDLAS measures the intensity loss of a diode laser beam tuned to a water absorption line that passes through a cell filled with the sample gas. This technique is capable of detecting low-ppb concentrations of moisture in a range of gases including hydrides such as NH₃⁵⁾. As NH₃ absorbs strongly in the infrared, the ultimate sensitivity depends on selecting an appropriate spectral region with weak NH₃ features where water absorption is strong, and accounting for any matrix contribution to the moisture measurement. The latter can be achieved using either a dual beam system equipped with a reference cell containing dry ammonia⁶⁾, or alternatively, by collecting a dry reference spectrum prior to sample measurement in a single cell for spectral subtraction. This work discusses the performance of a Delta F (Woburn, MA) 740 TDLAS

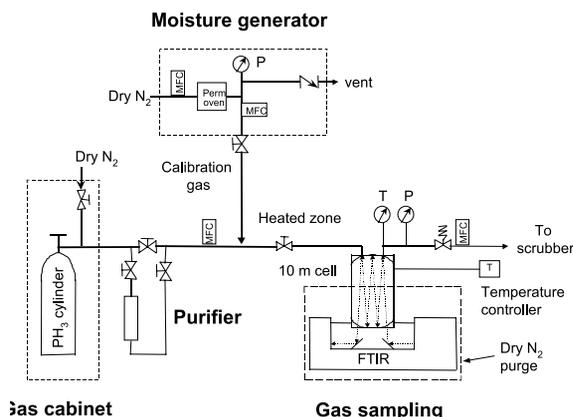


Fig. 1 Schematic of FTIR set-up used for calibration and analysis of moisture in phosphine.

analyzer for measurement of moisture in NH₃ with regard to instrument sensitivity, accuracy and stability. The instrument, which measures a water line at 1392.5 nm, was equipped with a 50m path length multi-path Herriott cell with an internal volume of ~1 L. Measurements in N₂ were performed at ~200 Torr and optimized response in NH₃ was obtained at ~70 Torr.

The Delta F 740 TDLAS analyzer was installed with a dilution manifold and moisture sources for calibration. As shown in Fig. 2, a vaporized liquid NH₃ stream containing a known amount of moisture was used for some of the measurements where small amounts of N₂ normally used to introduce moisture were interfering. The setup also included a vacuum pump for decreasing the sample pressure as line broadening at elevated pressures decreases sensitivity.

2.3 Cavity Ring-down Spectroscopy

CRDS is a relatively new spectroscopic technique based on the absorption of IR radiation that has been explored for detection of moisture at sub-ppb to ppm levels⁷⁻⁹⁾. An IR laser beam is directed into the ring-down cavity equipped with highly reflective mirrors that contains the sample gas. As the cavity fills with light, an increasing amount of the light leaks through the mirror into the detector. At a predetermined intensity of light reaching the detector, the laser beam is interrupted and the ringdown decay lifetime of the cavity is recorded (Fig. 3a). The moisture concentration in a sample gas is calculated from the following equation⁷⁾:

$$N = (1/\tau(\nu) - 1/\tau_{\text{empty}}) / (c \sigma(\nu))$$

where c is the speed of light, N is the molecular density or concentration of moisture, σ is the absorption cross section of water molecule in cm², $\tau(\nu)$ is the sample gas ring-down time, τ_{empty} is the ring-down time without moisture present and ν is the laser light frequency. As the total path length of the light beam inside the cell is in the range of kilometers, high sensitivity can be obtained. Additionally, the metal oxide based dielectric cell mirrors are highly corrosion resistant and thus are suitable for the measurement of aggressive gases such as HBr and Cl₂.

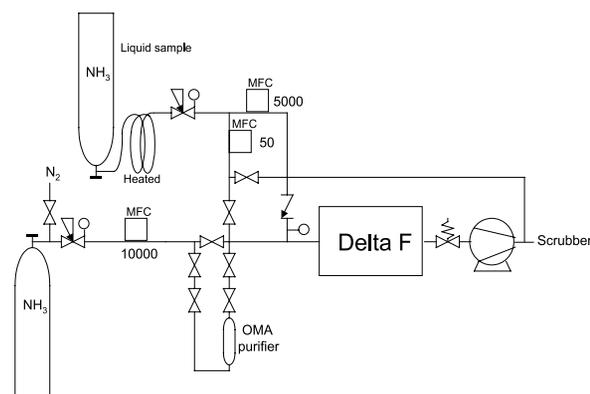


Fig. 2 Experimental setup for calibration and analysis of moisture in NH₃ by TDLAS.

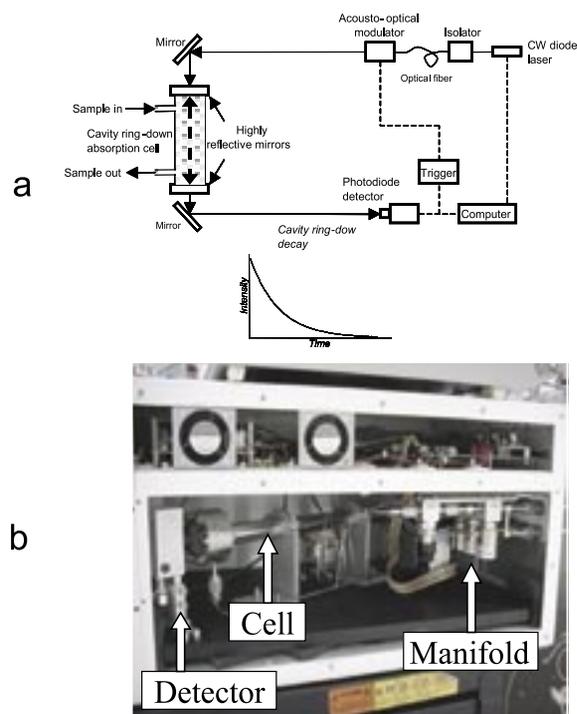


Fig. 3 Schematic of the components of CRDS and internal view of the Tiger Optics MTO-1000 CRDS instrument.

The tested instrument (MTO 1000, Tiger Optics (Warrington, PA)) scans the moisture spectrum in the range of 1390-1400nm by regulating the temperature of the laser diode. A photograph of the cavity with a volume of 250mL, detector and inlet system of the MTO 1000 is shown in Fig.3b. The manifold for calibration and cylinder analysis was similar to that shown in Fig.1 for the FTIR measurements. A 500mL Nanochem® MetalX purifier was used for purification of the sample gases, and calibrations were performed by adding nitrogen that was humidified with a moisture generator (Span pac 261, Kin-Tek (LaMarque, TX)) to purified HBr and Cl₂. The output concentration of the moisture generator was verified using a Buck Research (Boulder, CO) CR-3 chilled mirror hygrometer. The addition of N₂ to the sample gases caused a baseline shift that was compensated by a baseline-tuning scan. All measurements were performed at a flow rate of 1 slpm and a pressure of 110kPa.

3. Results

3.1 FTIR Spectroscopy for Moisture in Phosphine

Moisture absorbs in the mid-IR region at 3600-3900 cm⁻¹ and 1500-1900cm⁻¹ as shown in Fig.4. To maximize sensitivity, measurements with a Hg-Cd-Te detector were made in the lower wavenumber region with lower noise levels and background contributions from PH₃. Previous studies have shown that the sensitivity of the IR data can be maximized by lowering the spectral resolution and by performing spectral averaging. The FTIR was therefore programmed to average 512 spectra per data point at a resolution of 4 cm⁻¹. Calibration points were measured by

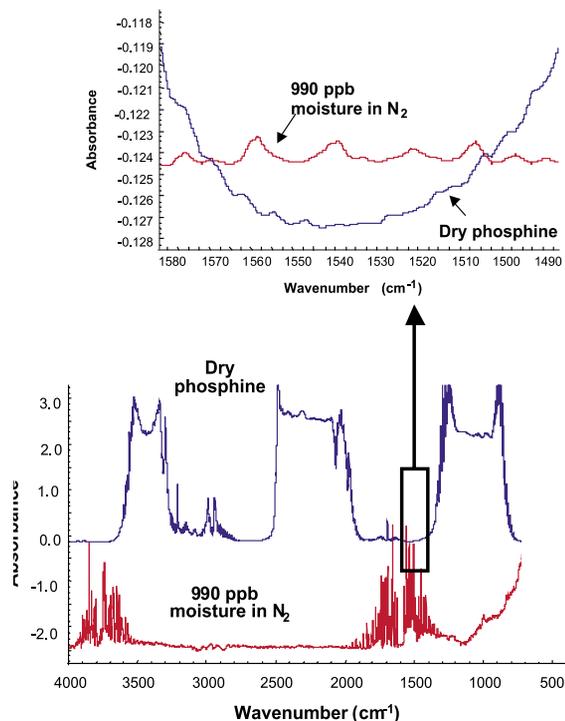


Fig. 4 IR spectra region used for moisture measurements in phosphine.

introducing moisture into dry phosphine from 99 ppb to 990ppb using the moisture generator. FTIR readings were equilibrated at each point for several hours and a linear calibration curve was obtained. The limit of detection based on ordinary least squares method calculated from the regression equation was 33 ppb⁽¹⁰⁾. It is likely that with further method optimization such as use of a narrow band-pass filter and operation at higher cell pressures, the detection limit could be lowered to ~10 ppb⁽¹¹⁾. It is also possible to obtain lower detection limit by using an InSb detector and a vacuum purging box that Taiyo Nippon Sanso Corp. has adopted.

The FTIR method has been adopted for routine measurement of trace moisture in Ultima 6N purity phosphine at Matheson Tri-Gas. It has also been used to characterize the efficiency of purifier media such as Nanochem® PHX for removal of moisture in phosphine (Fig. 5).

3.2 Tunable Diode Laser Spectroscopy for Moisture in Ammonia

The response of the TDLAS instrument in NH₃ was measured by adding moisture at low-ppb levels to a Nanochem® OMA purified NH₃ stream. When changing from N₂ purge to NH₃, an offset in the reading of ~150 ppb was observed. By instructing the acquisition software to collect an NH₃ background, the instrument could be re-zeroed. For better tracking of long-term drifts, the following measurements in NH₃ were performed without zeroing the instrument against an NH₃ background. Initial data showed that small amounts of N₂ that were used to introduce the moisture resulted in a false reading of ~10 ppb/% N₂ (Fig.6). This effect is likely due to broadening of

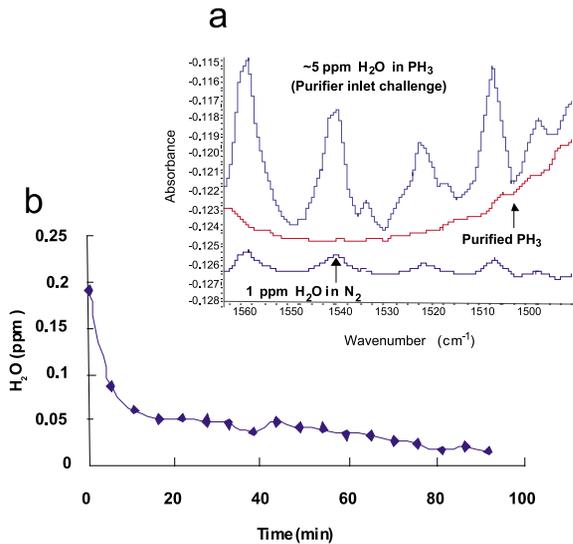


Fig. 5 (a) Dry down of a PH₃ line to below the FTIR detection limit using a Nanochem® PHX purifier as it is challenged with a 5 ppm moisture at 0.4 slpm and (b) IR spectra showing removal of moisture features in PH₃ by the purifier.

neighboring NH₃ peaks that were not accounted for by the instrument software. The response to N₂ complicates calibration as moisture addition is typically performed by mixing a humidified inert stream with the matrix gas.

Moisture was then introduced without co-adding N₂ by mixing a vaporized liquid NH₃ stream containing ~ 2.1 ppm H₂O with the purified NH₃. An example for such a calibration measurement is shown in Fig. 7. The instrument readout overestimated the concentration by ~ 20%.

The detection limit for H₂O in NH₃ matrix was estimated to be 9ppb based on 3 times the short-term signal/noise ratio (IUPAC⁷). Further experiments included stability measurements showed fluctuations in the range +/- 10ppb over several hours of operation, thus limiting true detection limits accordingly. Additionally, the lack of absolute verification methods for the moisture-free reference gas used in the spectral subtraction might add further uncertainty to these detection limits.

Also of importance is the control of pressure as broadening effects resulted in significant changes in the readings. According to the manufacturer, tight control at

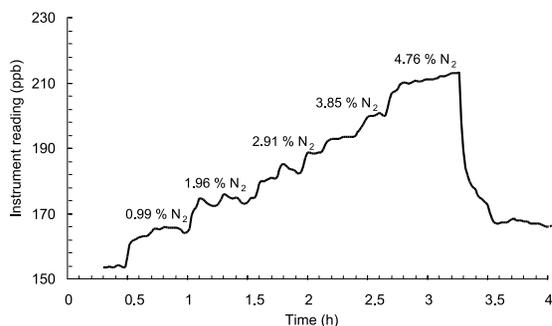


Fig. 6 Response of instrument to N₂ addition in NH₃ matrix without moisture.

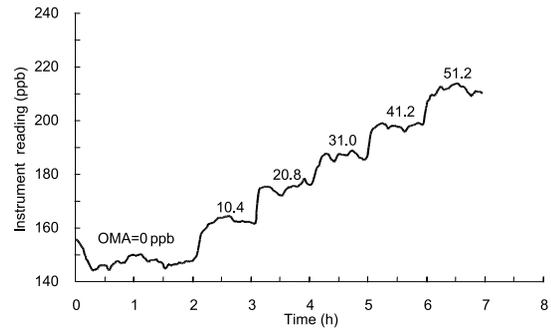


Fig. 7 Response of Delta F TDLAS analyzer to increasing moisture concentrations in N₂-free NH₃ stream.

~ 70Torr is required for optimized response. As shown in Fig. 8, deviation from these conditions can cause strong fluctuations in the instrument readouts.

Dry-down times were in the range of few minutes for concentration changes of ~ 100-200ppb and equilibration times for concentration increases were similar. This is demonstrated by the liquid phase analysis of a cylinder containing ~ 150ppb H₂O shown in Fig. 9. The system equilibrated within ~ 10-15 min.

3.3 Cavity Ring-down Spectroscopy for Moisture in Corrosive Gases

Fig. 10 shows spectra of moisture in Cl₂ and HBr gas matrices. The two moisture lines that can be used for quantification in the range of the MTO 1000 diode laser are at 1391.67 and 1392.54 nm, corresponding to a laser diode temperature of 21.15 and 29.64 °C, respectively. The instrument is capable of detecting moisture in N₂ from single ppb levels to 10 ppm.

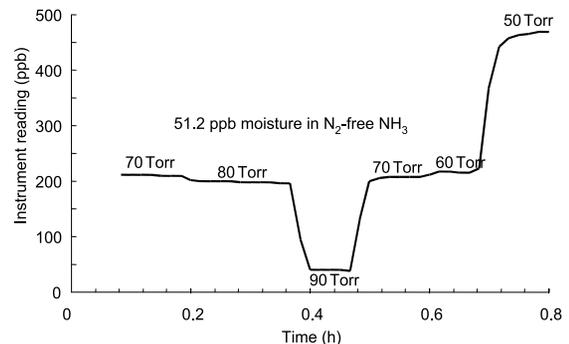


Fig. 8 Influence of pressure on the TDLAS reading at 51.2 ppb moisture in N₂-free NH₃.

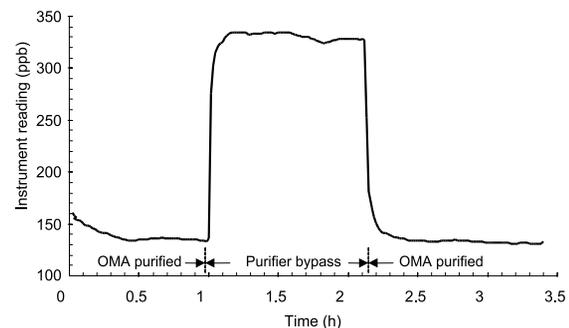


Fig. 9 Delta F 740 TDLAS reading of moisture concentration in liquid-phase ammonia from a cylinder source.

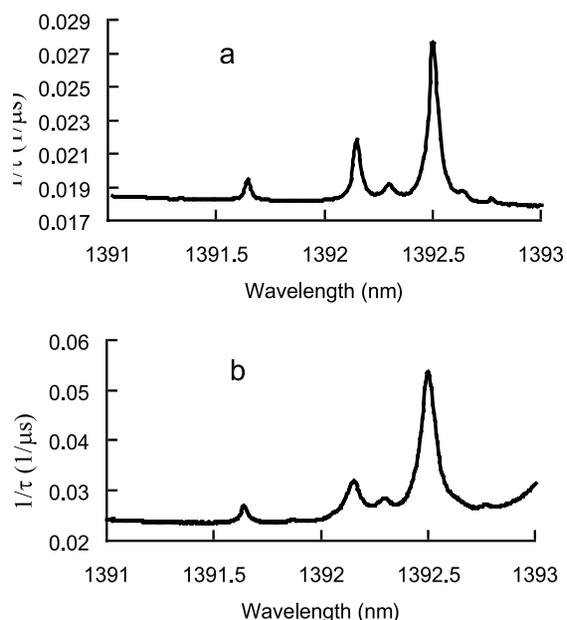


Fig. 10 CRDS spectrum of moisture in (a) Cl₂ and (b) HBr matrices.

A detection limit based on the signal/noise ratio of ca. 10 ppb H₂O in Cl₂ was obtained at the strong absorption peak (1392.54 nm). Calibrations in HBr and Cl₂ at the moisture line at 1391.67 nm showed a linear response. In Cl₂ matrix, moisture readings of the instrument overestimated the added concentration by ~16%. This discrepancy is likely caused by spectral parameters such as broadening coefficients in the instrument software that were not optimized for moisture detection in Cl₂. Measurements in HBr showed a curved baseline in the H₂O spectral region. Initially, the instrument software did not take the baseline shape into account resulting in an offset of the readings. A modified version of the data processing routines was then supplied by the manufacturer resulting in readings within ~3% of the actual moisture content. The MTO 1000 has been used to analyze moisture in several HBr and Cl₂ cylinder sources. Fig. 11 shows an example of such analysis for a Cl₂ cylinder that contained 104 ppb moisture in the gas phase.

The analysis of purified HBr and humidified HBr streams that were introduced through two different sample inlets was used to characterize both the response time to changes in moisture concentration and the efficiency of

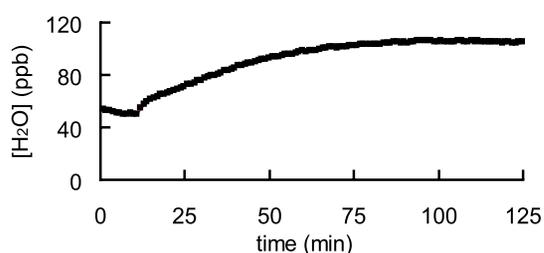


Fig. 11 CRDS detection of moisture in gas phase chlorine from cylinder source.

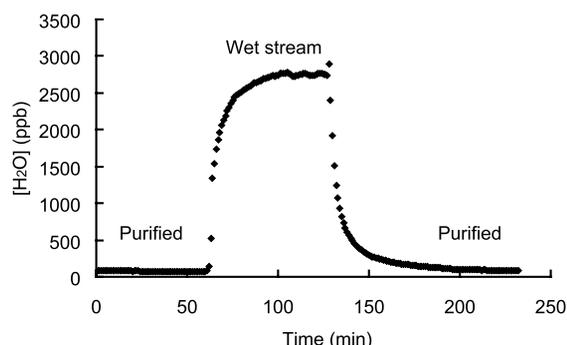


Fig. 12 CRDS measurement of moisture in alternated dry and wet HBr streams from two inlets during purifier testing.

the Nanochem® MTX purifier for moisture removal. The readings reached 90% of the final level within 20 minutes after switching between the purified and moist sample inlets. MTX reduced the moisture in the HBr and to <100 ppb (Fig. 12) when using ppm level moisture challenge.

4. Conclusions

Three commercial instruments for on-line moisture analysis in process gases using different spectroscopy techniques have been investigated. FTIR is the most universal instrument as a result of the wide spectral range that is accessible and has been shown to be suitable for moisture measurement of a few tens of ppb in a range of hydride gases including phosphine. The Delta F TDLAS instrument in contrast has been specifically designed as a stand-alone moisture monitor for ammonia process lines. Our studies demonstrate that this analyzer has a detection limit of 9 ppb. Although FTIR is also capable of detecting trace moisture in corrosive gases, previous studies have shown that the mirrors of currently available FTIR multi-pass gas cells are susceptible to corrosion, especially in HBr, resulting in loss of reflectivity in the time-frame of few weeks. The Tiger Optics CRDS instrument has shown to withstand the corrosive effects of gases such as HBr and Cl₂ over a test period of 6 month. This technique is sensitive to low ppb moisture levels and responds within a few minutes to concentration changes.

A common requirement for the three instruments is a moisture-free background for accurate spectral subtraction. Additionally, appropriate data analysis and calibration procedures are required for extracting accurate moisture concentration, especially in the presence of background interference and other spectroscopic artifacts such as pressure broadening or line broadening as a result of the presence of additional components in the gas stream. For both diode laser based techniques, the development of laser diodes with different spectral ranges where moisture absorbance is stronger and spectral interference from the matrix gas is minimized will be important to extend the applications and increase sensitivity in the future.

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