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Longevity Testing of a Prototype Discrete Dynode Detector For Triple Quadrupole Mass Spectrometer

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ABSTRACT

Purpose: Characterization of a new prototype detector for purposes of evaluation of life time and performance improvements for typical triple quadrupole mass spectrometer workflows

Methods: A modified Thermo Scientific™ TSQ Quantiva™ mass spectrometer was equipped with a prototype detector. The detector was tested utilizing an accelerated ageing approach through a developed automatic routine

Results: The prototype detector demonstrated impressive results in testing. Estimates based on heavy 24/7 instrument usage suggests a lifetime exceeding one year. The developed method provides a new tool and measure for evaluation of detector lifetime.

INTRODUCTION

Developments in MS technology have led to an increase in instrument throughput, thus elevating the ion current going to the detection system. The detector amplifies this current with the gain factor, allowing reliable detection of a single ion event. Contemporary detectors must have high dynamic range and be able to withstand extraction of significant output charge. Historically, the total charge accumulated by an Electron Multiplier (EM) over the entire lifetime is used as a measure of detector longevity. Prolonged detector lifetime is highly desirable, due to the benefits conferred to users. We have developed a method providing a new tool and measure for evaluation of detector lifetime and we have applied the method to a new prototype detector to evaluate improvements for typical triple quadrupole mass spectrometer workflows.

MATERIALS AND METHODS

Sample Preparation

PolyTyr 1,3,6 standard: in-house solution of 20 pmol/µL in HPLC grade Methanol: Water, 50:50 volume with 0.1% Formic Acid. Polytyrosine consists of L-tyrosine, (Tyr)3, (Tyr)6 from Sigma-Aldrich.

Test Method(s)

A modified TSQ Quantiva mass spectrometer was equipped with a prototype detector from ETP Ion Detect (Clyde, Australia). For evaluation purposes, an accelerated ageing approach was developed and a corresponding automatic routine was implemented. The key method element was interleaving of intense signal level scans with periods of quietness.

To further accelerate ageing, the incoming ion current was maximized and gain was increased up to 8X the standard value.

Longevity data collection comprised periods of interleaved scanning until a specified amount of charge was extracted from the multiplier. Upon reaching the specified charge value the system saved a record for elapsed time, extracted sample probe charge, extracted multiplier charge, etc.

After repeating of specified number of cycles described above the system performed electron multiplier calibration and then recorded new voltage values for MS and MSMS gains altogether with all other mentioned parameters.

Correlation analysis of time traces for charges extracted from sample probe and from multiplier provided good check for possible transmission problem or failed gain calibration.

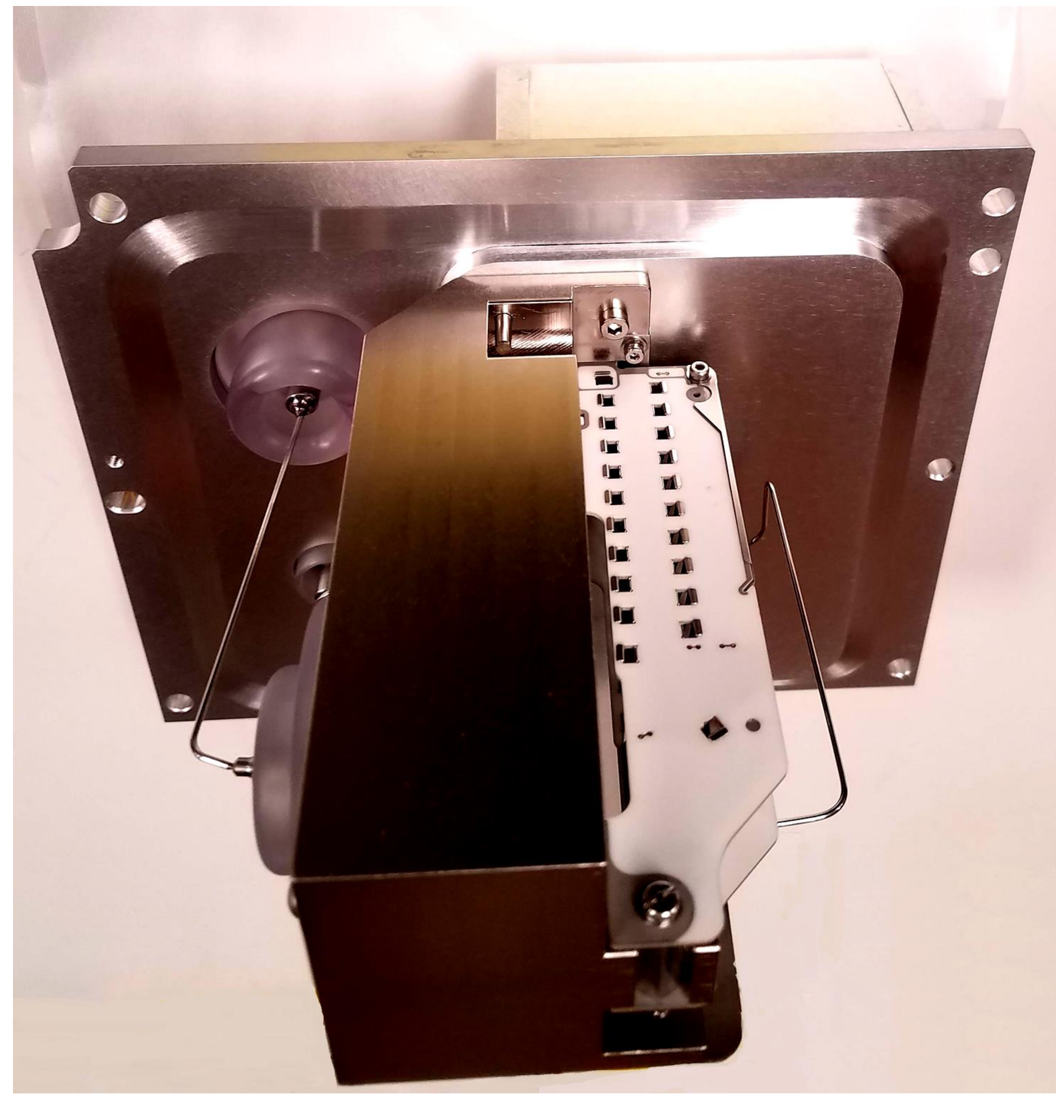
The dedicated diagnostic suite allowed programmed or manual control over many parameters of MS scans, incoming ion current and detector gain, experiment length, maintenance breaks, etc.

INSTRUMENT AND METHOD DETAILS

Details Of New Discrete Dynode Detector Design

The new prototype detector has been radically redesigned both mechanically and electrically compared to its predecessor. It benefits from new housing for high energy conversion dynode, 21 discrete dynode stages, pin-socket output connection and from design for precise and sturdy multiplier placement. With increased number of dynodes and optimized dynode shape, it offers extended voltage limit going up to -4500 V. The new detector assembly is shown on Fig.1.

Figure 1. New discrete dynode detector extends working voltage range by 1000 V as compared to its predecessor. The voltage extension of about 43%, combined with the increased number of dynodes, assumes longer multiplier life time.



Details Of The Method

The key method element was interleaving of intense signal level scans with periods of quietness. Following the suggestion of R&D scientists from ETP, the "resting" period was kept at 10 ms. Periods of 100 ms and 1000 ms were used for a while without any noticeable change in the instant ageing rate. Period shorter than 10 ms were not checked to prevent possible multiplier "self-cleaning", thus preserving the experiment consistency.

An MSMS (high) gain voltage was chosen for characterization of multiplier ageing and lifetime estimates because it approaches the absolute voltage limit first. Nevertheless, MS data were retained in the analysis for cross checks and comparison between low and high gain voltage evolution.

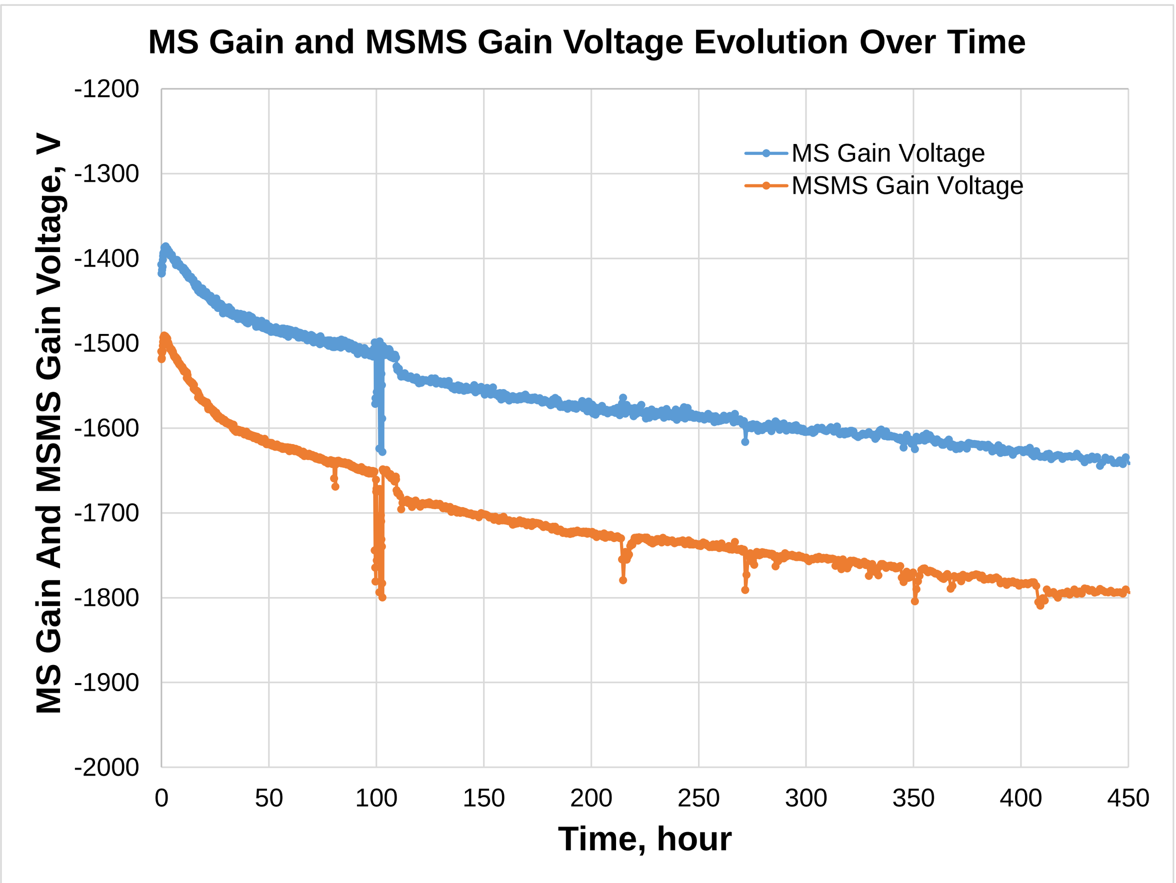
For quantitation purposes we introduced a new measure, the Ageing Rate (AR), equal to EM voltage change per extracted coulomb. This quantity can be used both for instant detector health characterization and for predictive purposes.

RESULTS

New Detector Life Time Estimates

The longevity testing was initiated on two modified TSQ Quantiva mass spectrometers as those instruments provide particularly bright ion beams. It should be noted that neither of instruments achieved the detector end of life. Both instruments demonstrated common features for multiplier ageing but one of them advanced much further; therefore, the data from that instrument will be used as a primary reference point. Fig. 2 below shows data from one of the longest "continuous" ageing measurement. As used herein, "continuous" denotes that no other activity occurred outside of maintenance or cleaning.

Figure 2. The longest "continuous" period of ageing measurements took about 19 days. The input ion flux varied from 5E7 i/s to 5E8 i/s.



Voltage spikes presented on plot above were caused by the technical problems resolved in the course of the experiment. The voltage discontinuities correspond to the moment of resolving of technical difficulties or instrument maintenance/cleaning.

The overall ageing rate of the new multiplier was estimated to be below 50 volt/coulomb. Estimates based on heavy 24/7 instrument usage with an average ion flux of 2E7 i/s, gain of 5E5 e/i and voltage range of 3300 V yielded a lifetime exceeding one year.

Comparison of these results with the data obtained earlier for the previous generation TSQ detector suggests that the new detector offers a significant lifetime improvement.

An interesting effect was observed at the beginning of the experiment, and it is illustrated on the Fig.3. Even with the proper vacuum conditioning, the detector was found to exhibit non-monotonic EM voltage evolution during the initial stabilization period. Later on, the voltages settled into a persistent and substantially monotonic ageing rate. Fortunately, the initial "burn in" period is not long and can be completely covered by the time the system requires for initial start up and calibration at the factory.

Another interesting effect was observed when both the gain and incoming ion flux were increased to values producing a signal close to the electrometer saturation level. We observed about 25-35 volts recovery of the potential for both MS and MSMS gain. The physics of the process is not clear yet. We speculate that it may be a vacuum cleaning process when very intense ion beam prevents migration of contaminants to the detector. Another conjecture is that relatively high electron current at final stages of multiplier "scrubs" contaminants already deposited to the dynode surfaces. The effect is illustrated on Fig.4.

Figure 3. Evolution of MS and MSMS gain voltages during initial "burn in" period.

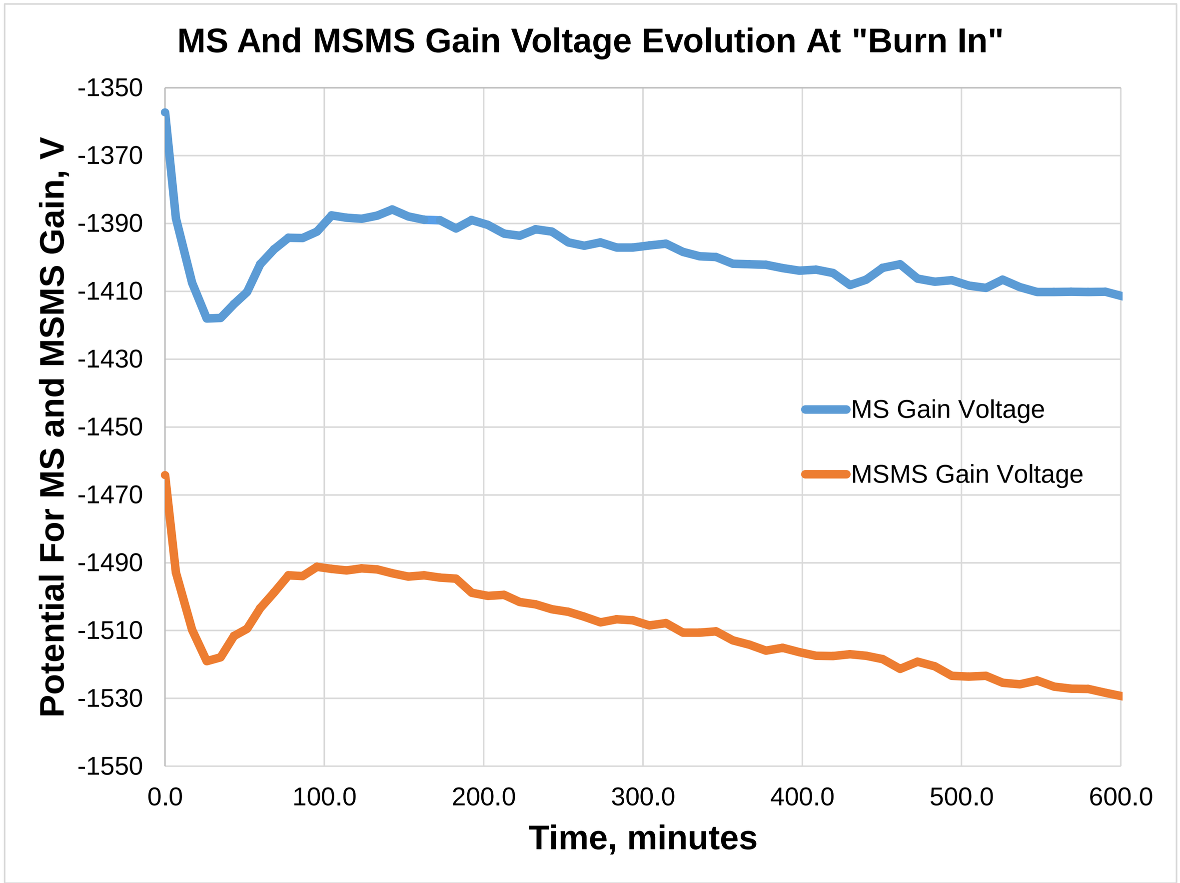
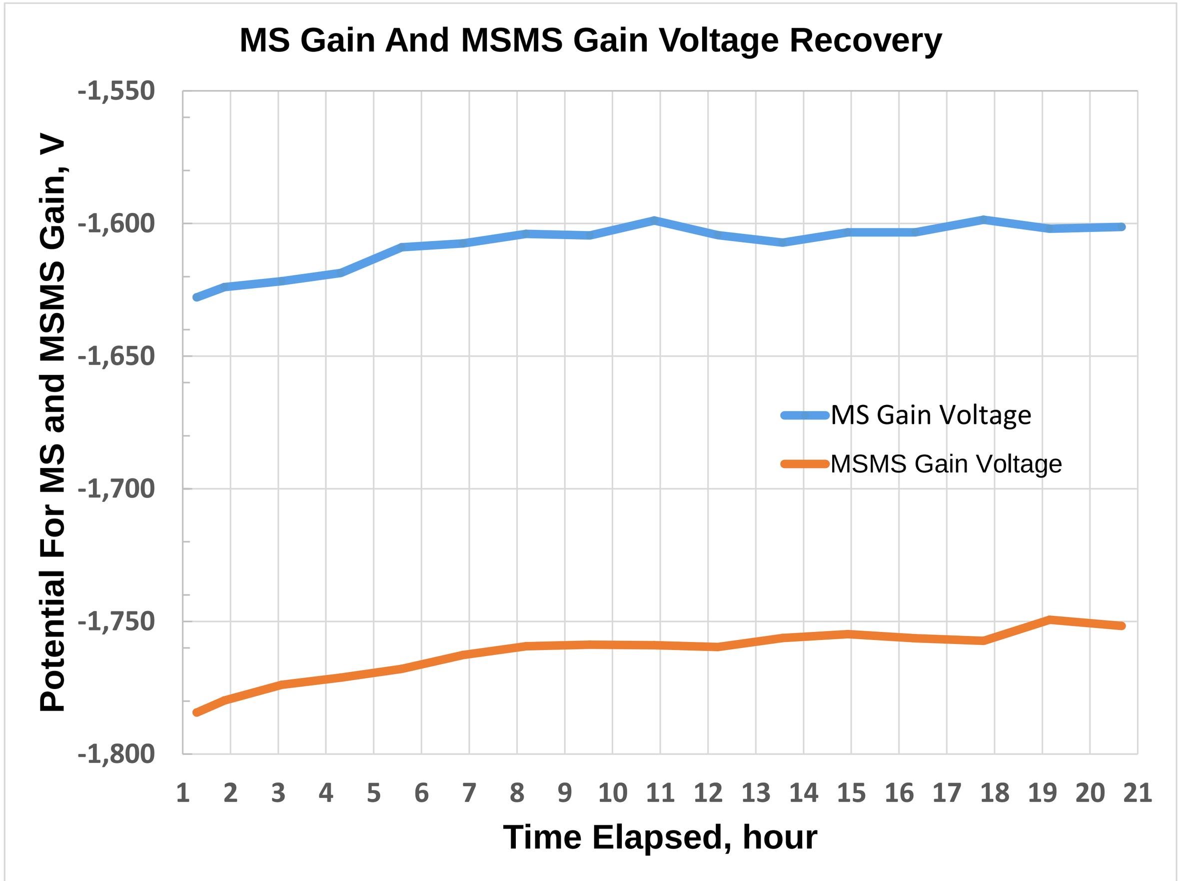


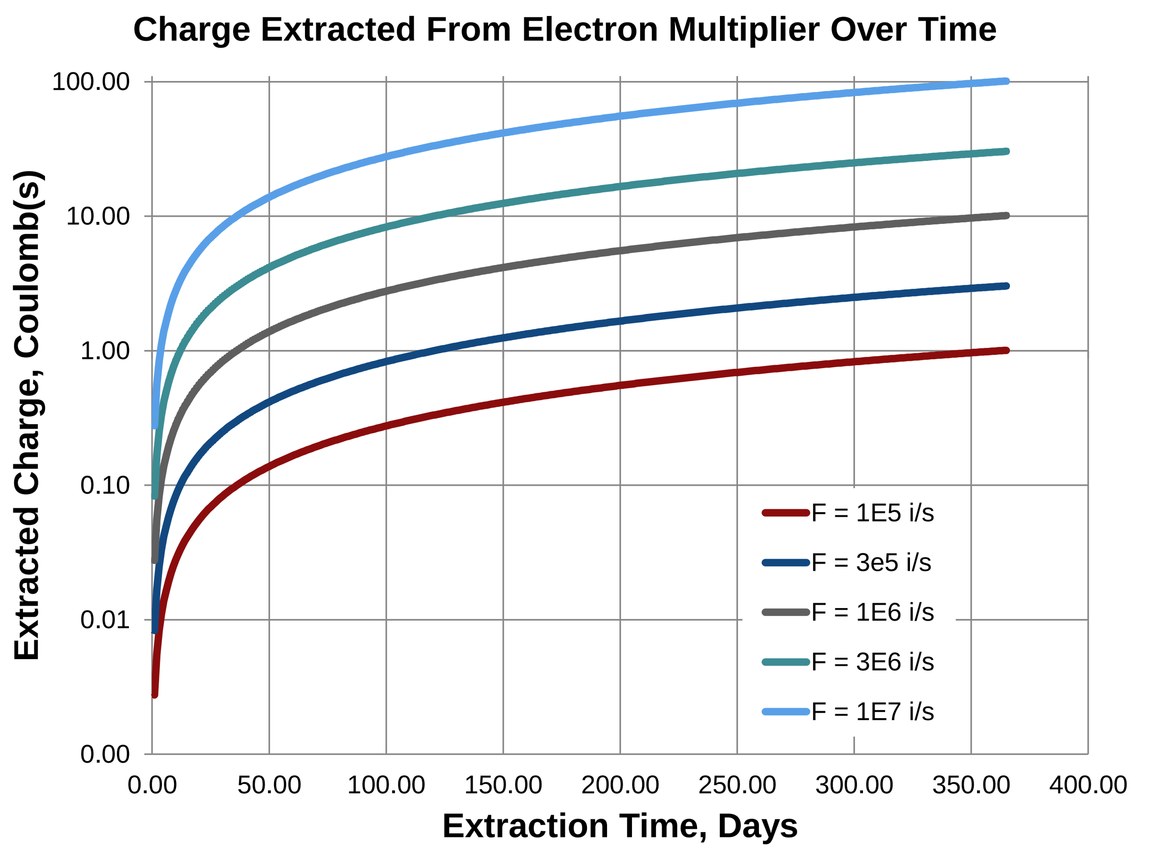
Figure 4. MS and MSMS gain voltage recovers 25 V to 35 V respectively when multiplier is exposed to high ion flux at 4E6 gain.



Is 1 Coulomb Still A Good Measure For Multiplier Life Time?

Historically, the total charge extracted from an EM over the entire lifetime is used as a measure of multiplier longevity. There exists a commonly held belief that a good estimate for multiplier life time is one Coulomb of aggregate extracted charge. The plot below demonstrates that such a statement may be correct under some circumstances, but that it does not generally hold for contemporary devices capable to output hundreds of microamperes of current. Even at a moderate ion load of 1E6 i/s, such devices must output about 10 Coulombs of charge over the course of one year.

Figure 5. The analytical estimates for charge extracted from electron multiplier at different values of incoming ion flux. The estimate is done on the assumption of continuous 24/7 sample infusion at the following parameters: multiplier gain is 2E6 e/i, incoming ion flux varies from 1E5 to 1E7 i/s, time is measured in days.



CONCLUSIONS

- The prototype detector demonstrated impressive longevity results in the test. Estimates based on heavy 24/7 instrument usage suggests a lifetime in excess of one year. Additional data points need to be taken at the end of detector lifetime to confirm the estimates and to complete the characterization.
- The introduced Ageing Rate measure, equal to multiplier voltage change per extracted coulomb, appears to be a convenient tool both for present detector health characterization and for overall lifetime estimation. It can be used for predictive purposes, as well, provided adequate data are collected to construct a database.
- The developed method provides a new tool and new measure for detector ageing study and lifetime characterization. As such it may be used for creation of one (or more) diagnostics tools for detector health check and for the "burn in" conditioning.

ACKNOWLEDGEMENTS

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TRADEMARKS/LICENSING

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