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Automatic Update of Electron Multiplier Gain Calibration Parameters in Polarity Opposite to the One Being Calibrated

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Overview

Purpose: To protect instrument from becoming inoperative because of weak or absent signal from the electron multiplier (EM) which experienced significant aging while EM gain calibration (EMGC) was maintained in only one polarity.

Methods: Analytical model and automated "calibration" routine were created and verified on the Thermo Scientific™ TSQ Quantiva™ triple-stage quadrupole mass spectrometer. The resulting routine was embedded into the instrument control software.

Results: Method ensures sufficient signal in the uncalibrated polarity upon completion of EMGC in the opposite polarity by updating the EMGC parameters for uncalibrated polarity using the predictive routine described below. This protects the instrument from becoming inoperative in a polarity with a "lagged" or outdated EMGC.

Introduction

In detection systems, a flux of incident ions hits the conversion dynode producing secondary particles which are received by the electron multiplier and amplified into a measurable signal. For positive ion polarity, the flux of secondary particles consists mostly of electrons, however, in negative ion polarity, these particles are positive ions. The difference in secondary particles necessitates an independent EM gain calibration for negative and positive polarities[1].

If the EM experienced significant aging and the calibration was maintained in only one polarity, the "lagged" EMGC parameters for the opposite polarity may result in a weak or absent signal which makes running the EM gain calibration impossible and prevents the use of the instrument in the affected polarity.

Methods

The proposed method resolves the aforementioned problems by employing the automated update of EMGC parameters for the polarity opposite to the one being calibrated.

Mass Spectrometry

Analytical model and automated routine were developed and verified on a TSQ Quantiva triple-stage quadrupole mass spectrometer.

Data Analysis

The method consists of an analytical model and an automated routine. The automated routine runs every time the EMGC runs. After completion of the EMGC in a given polarity, the routine builds an analytical model for the opposite polarity using the parameters it obtained from the calibration. The routine compares the modeled and current parameters for the non-calibrated polarity. If a specified update condition is met, the calibration parameters are updated using the rules specified in the model. Updating the non-calibrated polarity ensures the signal will be sufficient for operation or any necessary calibration procedures.

In developing the method, it was assumed that the slope of the EMGC curve for the non-calibrated polarity is not critically important and can be set equal to the slope from the polarity being calibrated. A second assumption was made about differences in positive and negative polarities in generation of flux of secondary particles from the dynode and conversion into electron current. It is proposed here that the difference can be minimized by appropriately setting the voltage offsets of the EM and the conversion dynode relative to ground potential.

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Results

Analytical Model

For analytical description of the problem, we assume that EM gain, *G*, can be described by the following function:

(1) $$G = A\exp\{BU\}$$

where *A* and *B* are calibration parameters and *U* is a voltage applied to the first stage of EM. Please note that the proposed formalism can be generalized to a class of functions of the form *G = G(A, B*U)*, where *A* is a normalization factor and *B* is a voltage scaling factor. Henceforth though, for the purposes of clarity, we will only use the explicit form of gain function given by Eq.(1) and consider one of two possible scenarios: the EMGC for negative polarity is outdated, the EMGC in positive polarity has just been completed.

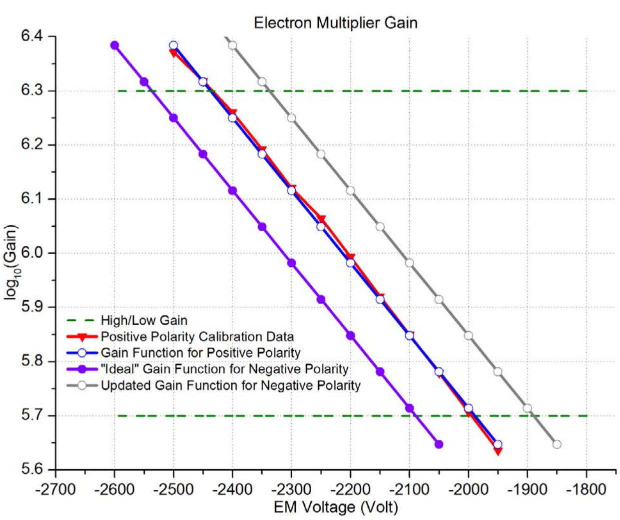
For two chosen points of this calibration, say, *LowGain* and *HighGain*, the following equalities hold:

(2) $$\begin{cases} G_{POS}(A^C_{POS}, B^C_{POS}, U^{CL}_{POS}) = LowGain \\ G_{POS}(A^C_{POS}, B^C_{POS}, U^{CH}_{POS}) = HighGain \end{cases}$$

where U^{CL}_{POS} , U^{CH}_{POS} are EM voltages corresponding to low gain and high gain, superscript *C* stands for "calibrated" (recently) and subscripts *POS* and *NEG* denote positive and negative polarity, correspondingly.

The difference between positive and negative polarities in generation of primary flux of secondary particles and converting them into electron current can be minimized by appropriately setting the voltage offsets of the EM and the conversion dynode relative to ground potential. The residual difference shows itself as different potentials applied to the first stage of EM in positive and negative polarities, both recently calibrated. We will denote its difference as a "shift" voltage, U_S . This voltage was estimated at the gain normally used for mass and resolution calibration and at the beginning of EMGC.

FIGURE 1. Results of positive mode calibration and corresponding "ideal" and updated gain functions derived for negative polarity. The shift voltage was taken equal to U_S = –100 V. The signal target for updated function was ~50%.



Thus, an "ideal" gain function for outdated negative polarity EMGC is just the gain function for recently completed positive polarity calibration shifted by U_S :

(3) $$G^i_{NEG} = A^C_{POS}\exp\{B^C_{POS}(U - U_S)\}$$

As we are further interested in calculations for one gain value only, we assume that the slope of *log₁₀ (G)* is not important and can be taken equal to the one from gain calibration in positive mode. The resulting "ideal" gain function is presented in Figure 1.

The next step is to calculate if the outdated calibration needs to be updated. In the course of calculations, it is assumed that signal intensity for outdated calibration is linearly proportional to the then current gain value. This allows substitution of signal comparison with gain value comparison, which allows to formulate the following condition for updating gain function:

(4) $$G^i_{NEG}(U^{Cold}_{NEG}) \le \alpha\, LowGain$$

where $\alpha < 1$ defines the fraction of the nominal gain triggering the update and the LHS is the ideal gain function estimated at U^{Cold}_{NEG} – the voltage corresponding to low gain in outdated calibration in negative polarity. In explicit form, the update condition takes the form:

(5) $$\exp\{B^C_{POS}(U^{Cold}_{NEG} - U^C_{POS} - U_S)\} \le \alpha$$

Inequality (5) may be expressed as a condition for voltage of the outdated calibration:

(6) $$\begin{cases} U^{Cold}_{NEG} \ge U^{THR}_{NEG} \\ U^{THR}_{NEG} = U^C_{POS} + U_S + \dfrac{\ln(\alpha)}{B^C_{POS}} \end{cases}$$

where U^{THR}_{NEG} is a threshold voltage triggering the update. When obtaining expression (6), it was accounted that calibration parameter B^C_{POS} and calibrated voltage U^{Cold}_{NEG} are negative values.

At the next step, we calculate the parameters which update the outdated calibration to a state satisfying two main conditions. First, update must deliver a signal which is good enough to see the calibrant peaks and to run mass or gain calibration. Second, the update must provide such a signal without multiplier overload.

Following the ideology for finding the update threshold voltage, U^{THR}_{NEG} , the target EM voltage, U^{TRG}_{NEG} , for satisfactory signal may be written as:

(7) $$U^{TRG}_{NEG} = U^C_{POS} + U_S + \frac{\ln(\beta)}{B^C_{POS}}$$

where β, ($\beta < 1$) is the ratio of acceptable signal to expected nominal signal. Then the values for updated calibration parameters A^{UPD}_{NEG} and B^{UPD}_{NEG} can be found when solving the equation:

(8) $$G^{UPD}_{NEG}(U^{TRG}_{NEG}) = LowGain$$

under assumption that the slope of $\log_{10}(G^{UPD}_{NEG})$ is equal to the slope of $\log_{10}(G^i_{NEG})$. Here and forward the superscript *UPD* stands for "updated."

For the explicit form of gain function given by Eq.(3), one immediately finds the following solutions for the case of outdated calibration in negative polarity:

$$\begin{cases} G_{NEG}^{UPD} = \beta^{-1} A_{POS}^{C} \exp\left\{B_{POS}^{C}\left(U - U_S\right)\right\} \\ A_{NEG}^{UPD} = \beta^{-1} \exp\left\{- B_{POS}^{C} U_S\right\} A_{POS}^{C} \\ B_{NEG}^{UPD} = B_{POS}^{C} \end{cases} \quad (9)$$

The resulting updated gain function for β ~ 50% is plotted in Figure 1.
Following the same method, the update condition and updated gain function for outdated calibration in positive polarity can be derived from results of recent calibration in negative polarity. The update condition gets the form:

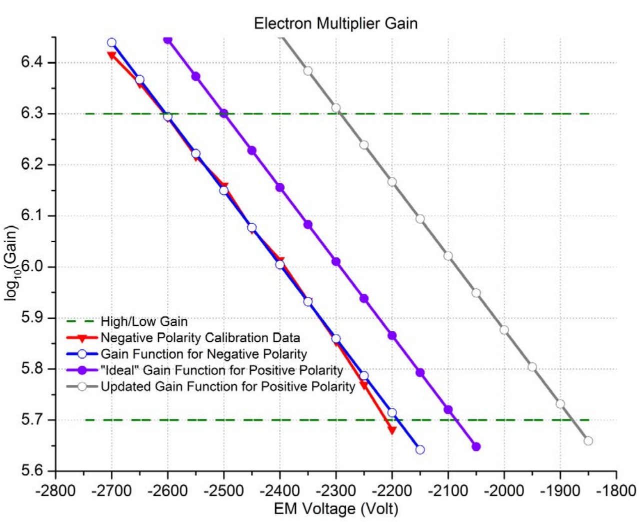
$$\begin{cases} U_{POS}^{Cold} \geq U_{POS}^{THR} \\ U_{POS}^{THR} = U_{NEG}^{C} + U_S + \dfrac{\ln(\alpha)}{B_{NEG}^{C}} \end{cases} \quad (10)$$

The corresponding updated gain function is expressed as:

$$\begin{cases} G_{POS}^{UPD} = \beta^{-1} A_{NEG}^{C} \exp\left\{B_{NEG}^{C}\left(U - U_S\right)\right\} \\ A_{POS}^{UPD} = \beta^{-1} \exp\left\{- B_{NEG}^{C} U_S\right\} A_{NEG}^{C} \\ B_{POS}^{UPD} = B_{NEG}^{C} \end{cases} \quad (11)$$

The results for simulation of updated gain function for positive polarity judging from results of recently completed EMGC in negative polarity are presented in Figure 2.

FIGURE 2. Results of negative mode calibration and corresponding "ideal" and updated gain functions derived for positive polarity. The shift voltage was taken equal to U_S = –100 V. The signal target for updated function was ~50%.



Experimental Verification

In the current experimental setup, the potential difference between the conversion dynode and the first stage of the EM comprised about +10 kV in positive ion polarity and about –14 kV in negative ion polarity. Multiple calibrations confirmed that in negative ion polarity, the first stage of the EM is usually set 100V to 200V more negative as compared to positive ion polarity. Therefore, the "shift" voltage U_S = ±100 V (sign depends on polarity) was used in building the simulated EM gain function for the non-calibrated polarity and used in calculation of the update condition.

In one implementation, the update engaged if the simulated gain estimated using the old calibration parameters fell below 10% of nominal gain. In this case, the new values for calibration parameters were calculated to set gain value at 50% of expected nominal gain.

The robustness of the method was confirmed by artificially changing the EM calibration parameters in the calibration file. The change resulted in a 1000-fold decrease of EM gain in the affected polarity and consequently in a weak signal, insufficient for mass or EM gain calibration. Performing EMGC on the artificially modified calibration file confirmed that the MS instrument was set into a state with well detected signal allowing the successful EM or mass and resolution calibration without overloading the multiplier and attached electronics.

Conclusions

- The developed analytical model allows for quantitative estimate of EM gain calibration parameters for polarity opposite the one being calibrated.
- The elaborated automated routine which runs every time the EM is calibrated compares modeled gain parameters with the then current ones for the opposite polarity, and updates them if the specified update condition is met.
- The described method protects the instrument from becoming inoperative in a polarity with "lagged" EMGC because of weak or absent signal.
- The method ensures that the MS instrument will be set into a state with well detected signal without overloading the multiplier and attached electronics.
- The general nature of the developed analytical model assumes that upon appropriate tailoring of parameters entering the model, the method may be applicable to EM based detection systems of different design.

References

1. Schoen, A.; John Syka, S. private communication, March 1989.

Acknowledgements

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