

## RESEARCH ARTICLE

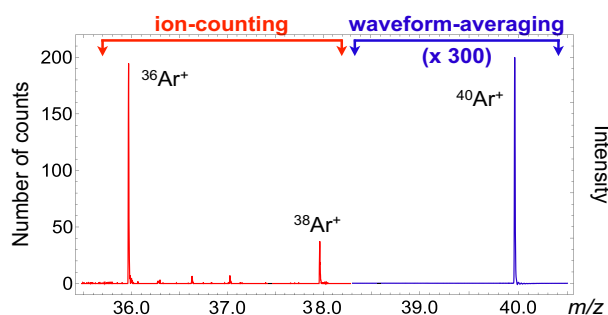
# Improved Quantitative Dynamic Range of Time-of-Flight Mass Spectrometry by Simultaneously Waveform-Averaging and Ion-Counting Data Acquisition

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**Abstract.** Two different types of data acquisition methods, “averaging mode” and “ion-counting mode”, have been used in a time-of-flight (TOF) mass spectrometry. The most common method is an averaging mode that sums waveform signals obtained from each flight cycle. While it is possible to process many ions arriving at the same TOF in one flight cycle, low-abundance ions are difficult to measure because ion signals are overwhelmed by noises from the detection system.

An ion-counting mode is suitable for the detection of such low-concentration ions, but counting loss occurs when two or more ions arrive at the detector within the dead time of the acquisition system. In this study, we introduce a technique that combines two methods to measure target ions with a high concentration difference, i.e., averaging mode and ion-counting mode are used simultaneously for high abundant and trace ions, respectively. By processing waveforms concurrently during data acquisition, one can choose to analyze either or both types of data to achieve a highly quantitative mass spectrum over a wide range of sample concentrations. The result of the argon isotope analysis shows that this method provides a more accurate determination of the isotope ratio compared to averaging mode alone at one-twentieth of the analysis time required by ion-counting alone.

**Keywords:** Data acquisition, High dynamic range, Isotope analysis, Time-of-flight mass spectrometry

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## Introduction

Data acquisition in conventional time-of-flight (TOF) mass spectrometers is performed by averaging ion current signals from a detector for each flight cycle [1]. “Averaging mode” with a high-speed digitizer can process many ions arriving at the same TOF in one flight cycle, the result of which is high sample throughput. However, the spectral quality is easily affected by the signal distortion and electrical noise from the detection system, which can compromise the quantitative

determination of peak area and height and cause errors in mass assignment [2]. In particular, for the case in which only a few ions are detected out of hundreds and thousands of flight cycles, ion signals are overwhelmed by the accumulated background noise, and thus, the ion peak cannot be observed in the averaged mass spectrum.

To detect such low-concentration ions, another type of detection method, “ion-counting mode” is suitable [1]. When a single-ion pulse signal exceeds a preset threshold, the time interval between the acceleration trigger and the single-ion pulse event are stored in the histogram data. After the accumulation of the time data over the course of the acquisition period, a TOF spectrum is created using the histogram of ion detection

events in each time bin. By setting the threshold value higher than the noise amplitude, noise is not incorporated into the spectrum, so that low-concentration ions can be measured with high quantitative accuracy.

In general, the ion-counting method is implemented with a time-to-digital converter (TDC). A disadvantage of this method is that counting loss occurs when two or more ions arrive at the detector within a dead time (a time during which the detection system is unable to respond to another ion after an ion detection event has occurred). The dead time of the current TDC technology has been improved to around 10 ns. Moreover, the software-based ion-counting technique used in this study has reduced the dead time to a single-ion pulse width, e.g., a few nano-seconds [3]. Nevertheless, when two ions reach the detector at the same TOF, the detection system records the event as a single ion-count. For this reason, ion-counting mode can be applied only to the measurement of low-concentration samples or condition in which ion production yield is adjusted so that less than one ion is detected per flight cycle. This leads to an increase in the measurement time and reduction of the sample throughput.

To compensate for these disadvantages, various types of ion detection methods combining averaging mode and ion-counting mode have been proposed [4, 5]. In this study, we have developed a new data acquisition method that calculates an averaged waveform and ion-counted histogram simultaneously from waveforms obtained in each flight cycle. By simultaneously collecting averaging mode and ion-counting mode data, a highly quantitative mass spectrum with large dynamic range can be attained within a short measurement time. For the purpose of performance evaluation, this method was applied to the isotopic composition analysis of atmospheric argon. In this paper, we first present the result of the ion-counting mode and then compare with the combination method in terms of analysis accuracy and measurement time.

## Experimental

The experiment was carried out using a miniaturized multi-turn TOF mass spectrometer (infiTOF-UHV, MSI-Tokyo, Inc., Japan) [6], with in-house modifications for timing control and data acquisition [2, 3]. The timing signals to the ion source, injection/ejection electrodes, ion gate, and digitizer were controlled by a delay/pulse generator built in-house on a DE0-nano-SOC development kit (Terasic, Taiwan). By controlling the ion gate timing, the unwanted ions are expelled from the mass analyzer, and the ions of the target mass range are selected. The ejection timing determines the number of laps of “multi-turn mode” of the mass analyzer [6], which corresponds to the flight path length for the target ions. The mass resolution of the analysis increases with the number of the laps.

The detected ion signal is amplified through a high-speed preamplifier (ORTEC model 9301, Advanced Measurement Technology, USA) and read out with a high-speed 1GS/s digitizer (U5303a, Keysight, USA). The readout waveform is passed into concurrent processing pipelines. Data processing is

conducted in 16 symmetric concurrent threads on a dual Intel 8-core Xeon processor PC with the Linux (Debian 8.6) operating system. All data acquisition is performed using open-source-software “QtPlatz” (<https://github.com/qtplatz>) with its plug-in developed for the infiTOF system.

In this experiment, ambient air was introduced directly into the electron ionization (EI) ion source via a 0.1-mm inner diameter  $\times$  1.0 m fused silica capillary at room temperature. Ions were produced by EI at the ionization voltage of 70 eV and accelerated into the mass analyzer at the repetition rate of 1 kHz. The production yield of ions was controlled by the emission current of the electron beam. The target ions of three Ar isotopes ( $^{36}\text{Ar}^+$ ,  $^{38}\text{Ar}^+$ , and  $^{40}\text{Ar}^+$ ) were selected with the ion gate and stored in the closed orbit of the mass analyzer. After 10 laps, the ions were ejected into the electron multiplier detector (14882, ETP Electron Multipliers, Australia) through the ejection electrode, and each waveform was acquired by the digitizer.

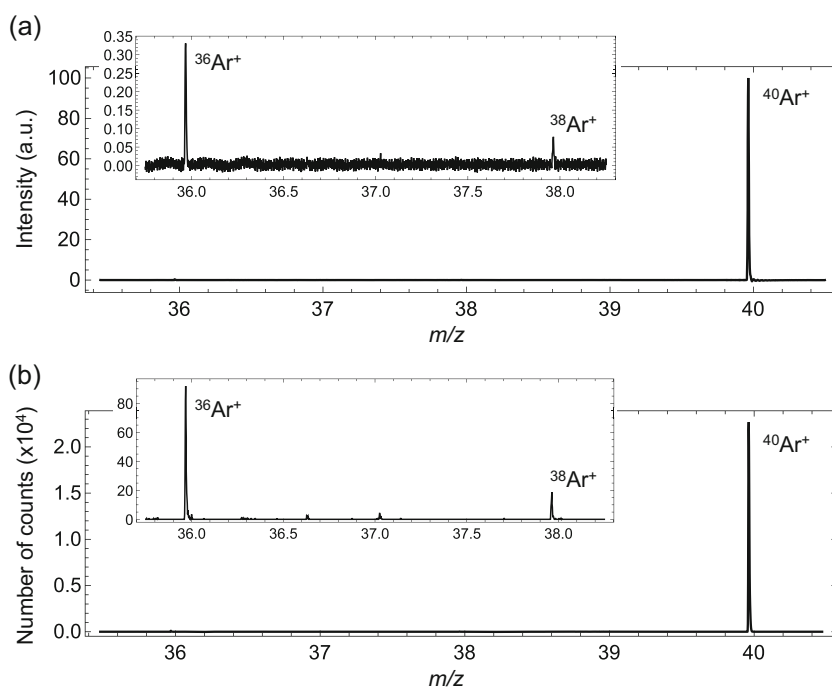
The waveform intensity is transformed into millivolts, and its baseline is adjusted to 0 V. The baseline level was determined by averaging a non-peak region of a waveform. This calculation improves the signal-to-noise ratio for the averaged spectrum [7]. The waveform is then brought into the two processes: one for averaging and one for ion-counting calculations. The averaging is carried out by summing waveforms up to the preset accumulation number and stored on a file as a function of elapsed time. The ion-counting is conducted by adding one count for each event in which ion pulse exceeds the threshold value on the waveform at 1-ns intervals. The TOF for each event is determined as the time point of the first local apex following the threshold. In the detection system, the most frequent pulse height of the single ion was around  $-30$  mV, while the peak-to-peak amplitude of the electrical noise was less than 3 mV without waveform-averaging, and the systematic noise was very low. Therefore, the threshold value set to  $-10$  mV is enough to separate the ion pulse signals from the noise.

## Results and Discussion

### *Isotope Analysis with Ion-Counting Method*

The argon isotope spectra obtained from the averaging mode and ion-counting mode are shown in Fig. 1. The number of the accumulated waveforms used was 200,000 in both cases. The mass resolution was around 5000 (FWHM) for  $^{40}\text{Ar}^+$  ( $m/z$  39.96).

For averaging mode data acquisition, the ion production rate was adjusted so that the detector was not saturated with the most abundant isotope ion signal,  $^{40}\text{Ar}^+$ . Under this condition, the count rate of  $^{36}\text{Ar}^+$  was 5% of total triggers over the course of the waveform accumulation. Considering the isotopic composition of terrestrial atmospheric argon [8] ( $^{36}\text{Ar}$ :  $^{38}\text{Ar}$ :  $^{40}\text{Ar}$  = 0.00334: 0.000630: 0.996), the count rate of  $^{38}\text{Ar}^+$  is less than 1%. Such low count rate means that a large fraction of the accumulated waveforms have no ion peaks; therefore, the resultant peak shape of the averaged spectrum was deteriorated by the noise from the mass analyzer, as shown in the inset of Fig. 1a. The skewed peak shape can result in error in the



**Figure 1.** Mass spectra of  $^{36}\text{Ar}^+$ ,  $^{38}\text{Ar}^+$ , and  $^{40}\text{Ar}^+$  obtained by averaging mode (a) and ion-counting mode (b). Each spectrum was obtained using 200,000 accumulated waveforms. Zoomed parts of each spectrum for less abundant isotopes are inset. The averaged spectrum of less abundant ions was affected by the noise from the detection system

determination of the peak centroid and compromise the quantitative analysis of the peak height and area.

For ion-counting mode data acquisition, the ion production yield was controlled in such a way that the count rate of  $^{40}\text{Ar}^+$  did not exceed 50%, above which ion-counting loss could occur [2]. Under this condition, the ion-count rate of  $^{38}\text{Ar}^+$  was too low ( $\sim 0.03\%$ ) to detect with averaging mode, whereas with the ion-counting mode, the  $^{38}\text{Ar}^+$  peak was clearly observed since the noise was not incorporated into the obtained spectrum (see inset of Fig. 1b).

The isotope ratios of  $^{40}\text{Ar}/^{36}\text{Ar}$  and  $^{38}\text{Ar}/^{36}\text{Ar}$  derived from the ion-counting spectrum are shown in Fig. 2. The data points were obtained from the accumulated spectra of both 200,000 and 400,000 waveforms. At a data acquisition rate of 1 kHz, the measurement time to take one data point were 200 and 400 s for 200,000 and 400,000 accumulations, respectively. The isotope ratios are scaled as delta values, deviations relative to the terrestrial argon isotope ratio in per mil (‰), which are defined as

$$\delta^i\text{Ar} = \left[ \frac{\left( \frac{i\text{Ar}}{^{36}\text{Ar}} \right)_{\text{observation}}}{\left( \frac{i\text{Ar}}{^{36}\text{Ar}} \right)_{\text{terrestrial}}} - 1 \right] \times 1,000 (i = 38, 40) (\text{‰}).$$

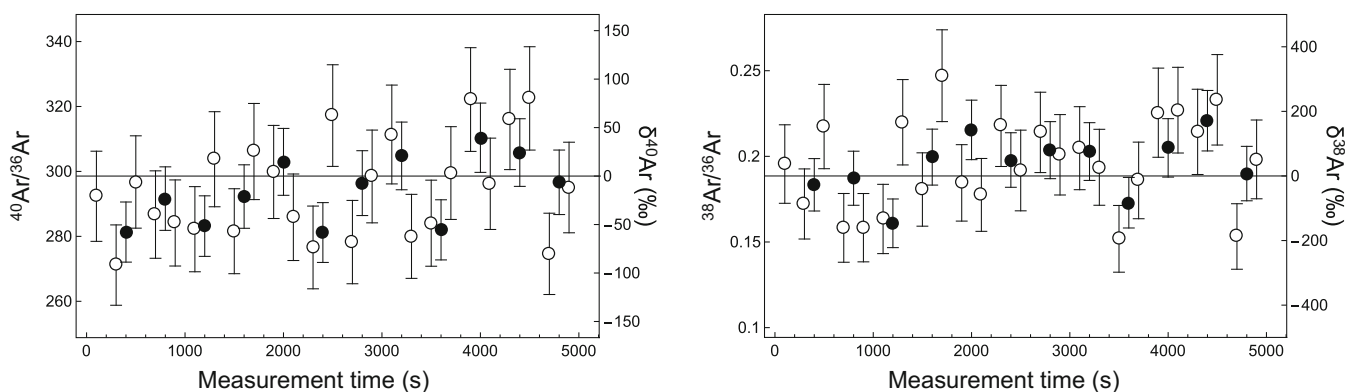
The error bars indicate  $1\sigma$  estimated by error propagation and the uncertainties in the counting statistics described below. Both  $^{40}\text{Ar}/^{36}\text{Ar}$  and  $^{38}\text{Ar}/^{36}\text{Ar}$  are consistent with the terrestrial values within  $2\sigma$ , though slight periodic time variations are observable.

According to Poisson statistics, the measurement uncertainties are the square root of the total ion-count. Therefore, the uncertainties of the results of the 400,000 waveforms (33 ‰ for  $^{40}\text{Ar}/^{36}\text{Ar}$  and 86 ‰ for  $^{38}\text{Ar}/^{36}\text{Ar}$ ) are  $\sqrt{2} \sim 1.41$  times smaller than those obtained from the 200,000 waveform sample (47 ‰ for  $^{40}\text{Ar}/^{36}\text{Ar}$  and 121 ‰ for  $^{38}\text{Ar}/^{36}\text{Ar}$ ). In the  $^{40}\text{Ar}/^{36}\text{Ar}$  measurement, the reduced  $\chi^2$  values of the dispersion of the data points relative to the measurement uncertainties are 1.18 and 1.13 for 200,000 and 400,000 accumulations, respectively. This result indicates that the variations are within the counting statistics error.

It follows from this result that a higher precision analysis will be accomplished by increasing the number of waveform accumulations. However, this also means that the measurement time will be longer than several minutes for one analysis. It is unfeasible to apply this kind of monitoring to rapid temporal gas composition variations or analysis of a small amount of sample (e.g., [3, 9, 10]). To shorten the measurement time while maintaining analytical precision, we introduced the combination method in which high-abundance ions are measured by averaging mode, and trace-level ions are detected by ion-counting mode.

### Isotope Analysis with Simultaneous Data Acquisition Method

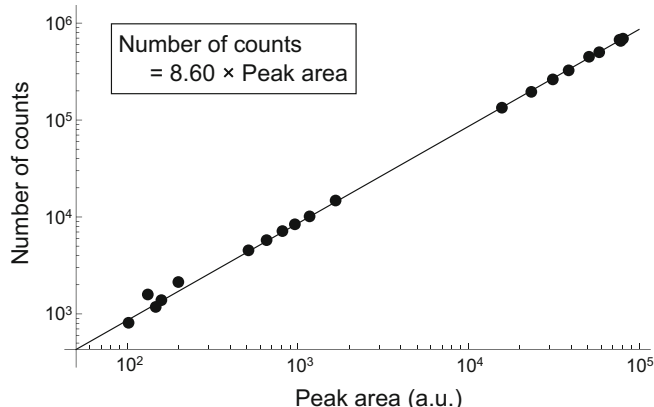
Figure 3 shows the relationship between the peak area calculated from the waveform-averaged spectra and the number of counts obtained using ion-counting mode. The data points are



**Figure 2.** Argon isotope ratios of  $^{40}\text{Ar}/^{36}\text{Ar}$  (left) and  $^{38}\text{Ar}/^{36}\text{Ar}$  (right) derived from the ion-counting spectra. The spectra were calculated using 200,000 waveforms (open circles) and 400,000 waveforms (black circles), the measurement times of which were 200 and 400 s, respectively. One hundred seconds are subtracted from the measurement time of open circles in order to make them more visible. The isotope ratios are scaled as delta values (‰) on the right vertical axis. The horizontal lines are the ratios of the terrestrial argon isotopes. The error bars are  $1\sigma$  uncertainties in the counting statistics

those selected from the  $^{36}\text{Ar}^+$ ,  $^{38}\text{Ar}^+$ , and  $^{40}\text{Ar}^+$  peaks measured at a count rate below 50%. The peak area was determined above 50% peak intensity to reduce the effect of noise on the peak shape. A linear relationship ( $R^2 = 0.999$ ) was observed, though the deviation increases with decreasing number of counts, because the peak shape of the averaged spectra taken at a low count rate ( $< 1\%$ ) was deteriorated by noise. Using the slope of the linear regression line (8.60), the peak area obtained from the averaging mode can be converted to the number of counts. This calibration line depends on a pulse height distribution of the detector for single ion event. Therefore, the same relationship can be obtained as long as the detector performance is maintained.

In the next measurement, the count rate of  $^{36}\text{Ar}^+$  was set at 5%, so that around 15  $^{40}\text{Ar}^+$  ions arrived at the detector for each accelerating trigger. Less abundant  $^{36}\text{Ar}^+$  and  $^{38}\text{Ar}^+$  ions were detected using ion-counting mode, while high-abundant  $^{40}\text{Ar}^+$  was measured by averaging mode and the peak area was

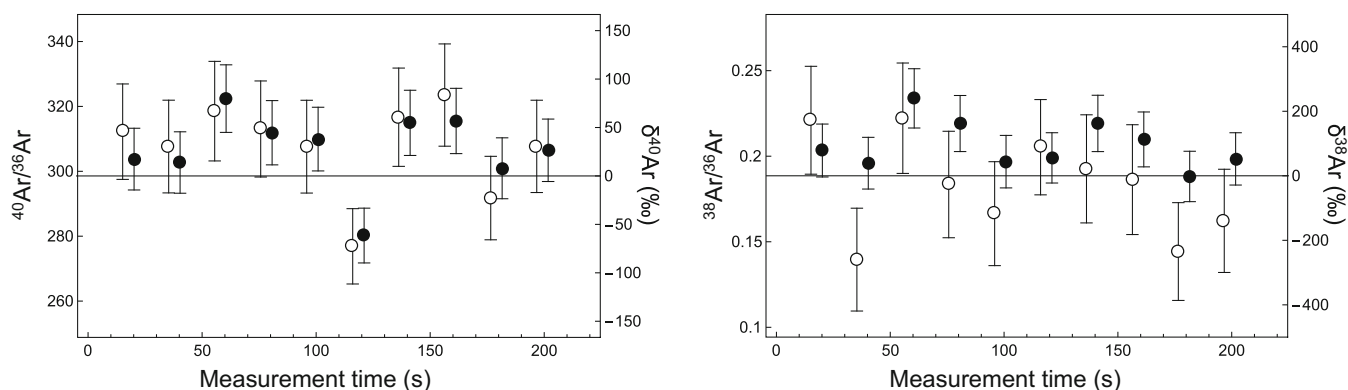


**Figure 3.** The relationship between the peak area of the averaged spectrum and the number of counts measured with ion-counting mode. A linear relationship ( $R^2 = 0.999$ ) was preserved even at three orders of magnitude. The slope of the linear regression line is 8.60

converted to the number of counts using the calibration line derived above.

The resulting isotope ratios of  $^{40}\text{Ar}/^{36}\text{Ar}$  and  $^{38}\text{Ar}/^{36}\text{Ar}$  obtained by the simultaneous data acquisition method are shown in Fig. 4. For comparison, the results of the averaging mode data analysis are also plotted. Each data point was obtained from the accumulated spectra of 20,000 waveforms collected over 20 s. The uncertainties in the combined methods were derived from the counting statistics (i.e., the square root of the total count), while those of the averaging mode were determined from the standard deviation of 10 measurements. As can be seen in Fig. 4, the measurement errors of the combined methods are smaller than those of the averaging mode. Specifically, in  $^{38}\text{Ar}/^{36}\text{Ar}$  measurement, the  $1\sigma$  values calculated from the simultaneously acquired data are roughly half as much as those of the averaged method alone, since the peak shape of  $^{38}\text{Ar}^+$  measured by the averaging mode was severely affected by noise at such a low count rate ( $< 1\%$ ), resulting in deterioration of the accuracy of the peak area determination.

Compared with the ion-counting mode (see Fig. 2), the uncertainties in the combination method with 20,000 waveforms are consistent with those of ion-counting with 400,000 accumulated waveforms. Though there appeared to be a systematic deviation from the terrestrial isotope ratio, the result indicates that the simultaneously collecting averaged waveform and ion-counting data can shorten the measurement time down to one-twentieth compared to ion-counting mode alone while maintaining the same measurement accuracy. The systematic deviation was probably caused by the instrumental mass fractionation that occurred in the ion source due to the electrostatic interaction between the produced ions. Following the previous study [3], this deviation can be corrected by measuring a reference sample under the same experimental condition.



**Figure 4.** Argon isotope ratios of  $^{40}\text{Ar}/^{36}\text{Ar}$  (left) and  $^{38}\text{Ar}/^{36}\text{Ar}$  (right) derived from the averaging mode (open circles) and the combined methods (black circles). The spectra were calculated from 20,000 waveforms. Five seconds are subtracted from the measurement time of the averaging mode in order to easily compare the two methods. The isotope ratios are scaled as delta values (‰) on the right vertical axis. The horizontal lines are the ratios of the terrestrial argon isotopes. The  $1\sigma$  error bars for the averaging method are the standard deviation of 10 measurements. The uncertainties for the combined methods are estimated from the ion-counts

## Conclusion

This study is intended to confirm the effectiveness of simultaneously collecting waveform-averaging and ion-counting data in a TOF mass spectrometry. For the quantitative analysis of low-abundance ions, ion-counting mode is applied to eliminate noise deterioration of the ion peak shapes. The quantity of high-abundance ions arriving in the same flight cycle is measured using the averaging mode.

The argon isotope ratios in the ambient air were measured using the combination method in which less abundant  $^{36}\text{Ar}^+$  and  $^{38}\text{Ar}^+$  were detected by ion-counting, and high-abundant  $^{40}\text{Ar}^+$  was measured by the averaging mode. The result shows that simultaneously using both methods provides a more accurate quantitative analysis of the isotopic composition than those obtained by averaging mode alone at one-twentieth of the measurement time of ion-counting mode alone.

This method enables the analysis of either or both types of data for any target ions. The effectiveness of each type of data depends on the ion abundance during the measurement; however, because the data for each method is acquired simultaneously, adjustment of the ion production yield to avoid the counting loss inherent in the ion-counting mode is not necessary. In this experiment, the averaging mode is applied for the count rate above 50%.

This method also has the potential to achieve a quantitative spectrum with an even wider dynamic range than that demonstrated in this study (more than three orders of magnitude,  $^{40}\text{Ar}/^{38}\text{Ar} \sim 1600$ ). Furthermore, if this method was implemented with firmware-based processing (e.g., on FPGA) instead of software-based processing with a high-performance PC, on-site analysis could be realized with a low weight and low power consumption system.

## Acknowledgements

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