

Noble gas MS

Emission Suppression Technology: revolutionizing noble gas isotope analysis



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Goal

The novel Emission Suppression Technology (EST) for the Thermo Scientific™ Thermo Scientific™ Argus VI™ Static Vacuum NG-MS revolutionizes noble gas isotope ratio mass spectrometry by negating the requirement to extrapolate back to t_0 . This technical note details how EST pauses sample consumption, allowing measurements to be made on properly equilibrated samples, resulting in dramatic improvements in both accuracy and precision of noble gas isotope ratios.

Introduction

Static vacuum mass spectrometry suffers from the problem that sample ionization starts immediately after introduction to the source and before isotopic equilibrium is reached. As ionization efficiencies of different isotopes vary, the isotopic composition of the sample being measured evolves with time (Figure 1). This presents a challenge when attempting to derive the isotopic ratio of the original gas sample. The solution to this problem in noble gas mass spectrometry (NG-MS) is to take a series of measurements after waiting an equilibration time and then extrapolating the isotope ratios back, to determine what the original isotopic composition of the gas would have been if it had entered the source fully equilibrated (Figure 1). This extrapolation comes at the cost of accuracy and precision, with decreasing precision the longer the time between sample introduction and first measurement. Furthermore, it has been demonstrated that changing the equilibration time can have an effect on the accuracy of the isotope ratio (Figure 2).

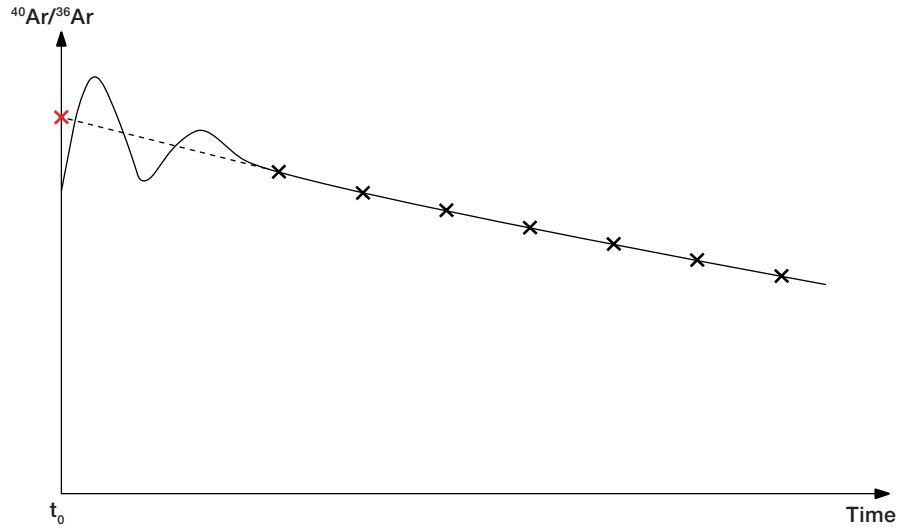


Figure 1. Schematic of $^{40}\text{Ar}/^{36}\text{Ar}$ ratio through time using traditional NG-MS, showing how sample is consumed before the sample is equilibrated. In order to derive the original $^{40}\text{Ar}/^{36}\text{Ar}$ ratio of the sample, the measurements must be extrapolated back to t_0 .

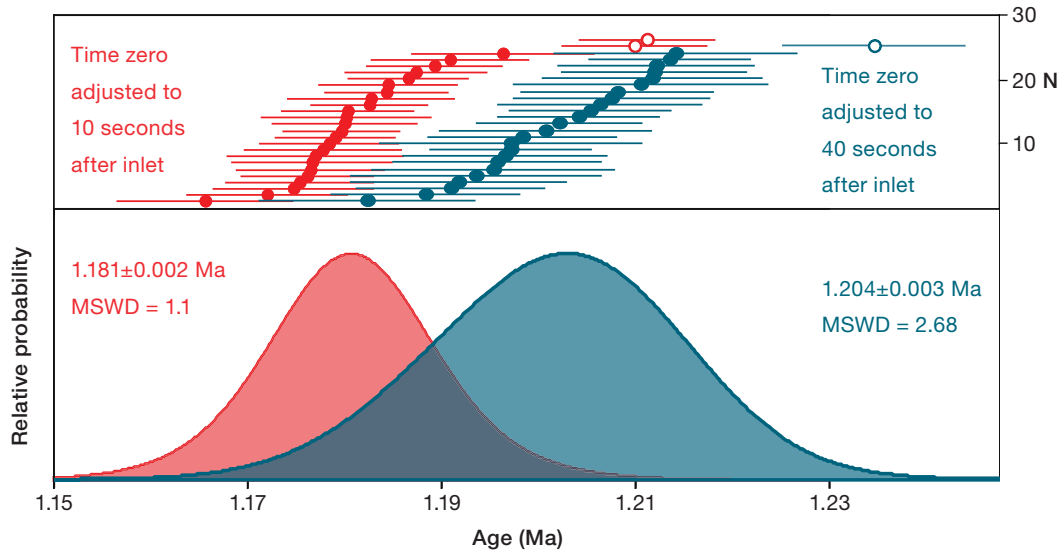


Figure 2. Ar-Ar dating of standard material showing the difference in final age depending on the length of equilibration time before first measurement. Source: Matthew Heizler, New Mexico Institute of Mining and Technology.

The novel Emission Suppression Technology (EST) completely transforms noble gas isotope ratio mass spectrometry. With EST, it is possible to switch off ionization until the sample gas is fully equilibrated in the source. This means that when ionization is triggered, the sample being measured will be unfractionated, enabling the first measurement to be made at t_0 .

How does EST work?

As we know, changing ion source conditions results in signal instability and in some instances can significantly affect the lifetime of the filament. Therefore, approaches such as turning the filament or accelerating voltage off and on are not appropriate. Also, due to the tactics utilized for controlling the emission current of electron impact ionization sources, in general, maintaining

constant environmental conditions within the ionization volume is a significant challenge. EST works by decreasing the electron energy below the ionization threshold of the gas of interest. This means that no ionization occurs as the sample is introduced (dark phase). With EST, the signal stability either side of the dark phase is reproducible within 0.1% (Figure 3). This signal reproducibility and stability demonstrates that the environment of ionization is perfectly maintained during the dark phase. Furthermore, switching does not impact the lifetime of the filament, and the switching from the dark phase to the measurement phase is very fast (<1 s) meaning no consumption/fractionation occurs prior to data acquisition; a true t_0 measurement.

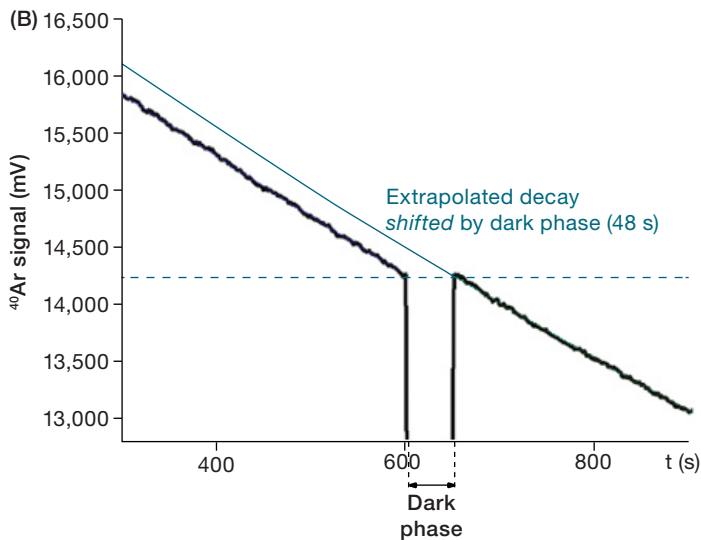


Figure 3. ^{40}Ar signal through time with 48 s dark phase in which the ionization energy was reduced below threshold using EST. Notice, no signal overshooting or undershooting after the dark phase.

Advantages of EST

EST results in dramatic improvements in both precision and accuracy of NG-MS. Furthermore, it opens the door to new developments in smaller volume, higher sensitivity preparation and gas generation systems.

The transient decreasing signal intensity of NG-MS has a significant impact on the precision of the measurement. The longer the waiting time for the sample to equilibrate in the source, the larger the uncertainty in the estimation of the original gas isotope ratio (Figure 4 – red points). EST removes this source of uncertainty because gas is not consumed during the equilibration phase. No matter the length of the equilibration phase, the precision remains unchanged (Figure 4 – blue points). With EST, the user has complete control over the design of the experiment, allowing equilibration times to be as long as required without affecting precision.

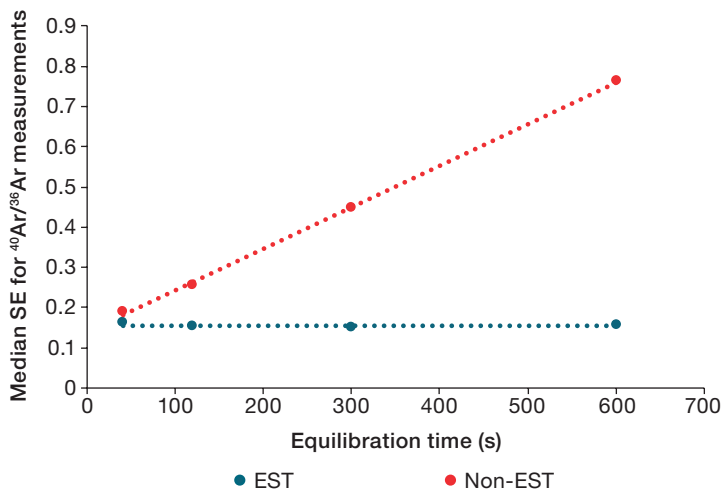


Figure 4. Effect of equilibration time on the precision of $^{40}\text{Ar}/^{36}\text{Ar}$ ratios for traditional NG-MS (red) and EST (blue). With EST the length of equilibration time has no effect on the precision of the isotope ratio.

Another major advantage of EST is improvements in the accuracy of the original isotopic ratio. For traditional NG-MS isotope ratios, there is an effect on the inferred isotopic ratio at t_0 with increasing equilibration time. For $^{40}\text{Ar}/^{36}\text{Ar}$, this has the effect of decreasing the $^{40}\text{Ar}/^{36}\text{Ar}$ ratio at t_0 by 0.06% per minute of equilibration time (Figure 5). With EST, the inferred ratio at t_0 is unaffected by equilibration time because the sample is not consumed during equilibration.

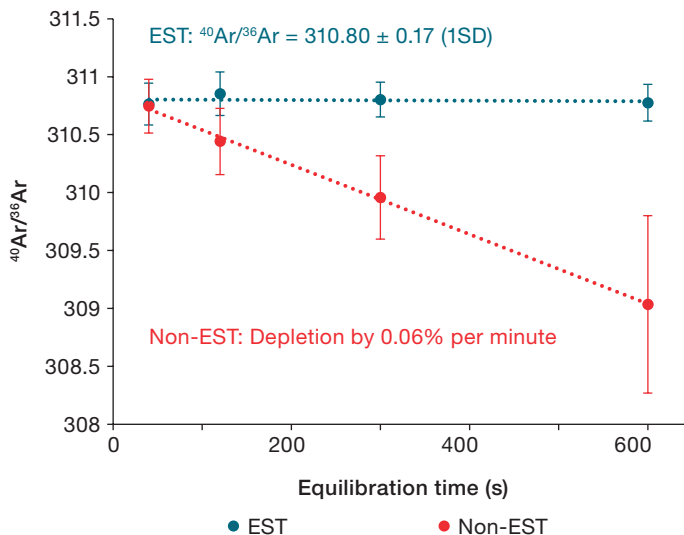


Figure 5. Effect of equilibration time on the accuracy of $^{40}\text{Ar}/^{36}\text{Ar}$ ratios for traditional NG-MS (red) and EST (blue). With EST, the length of equilibration time has no effect on the accuracy of the isotope ratio.

The gains in precision observed on air samples are mirrored in real rock samples. Here, sanidine samples from Alder Creek with an Ar-Ar age of 1.193 ± 0.001 were analyzed with and without EST using a 20 s equilibration time and 25 minutes analysis time. The comparison in terms of precision of the absolute $^{40}\text{Ar}/^{36}\text{Ar}$ ratios are shown in Figure 6. There is a >40% improvement in the precision of the final Ar-Ar date, which is attributed to the higher number of counts measured on ^{36}Ar as a result of not consuming sample during equilibration. These results illustrate that it would be possible to halve the sample size, or halve the analysis time and still achieve comparable levels of precision.

It should be noted that these experiments were conducted using a prep system and experiment procedure that has been established for non-EST analysis, i.e. very short equilibration times. The improvements in precision can therefore be viewed as very conservative examples of the typical improvement in precision offered by EST. With EST, there is the possibility for prep system and experiment procedure modification, for example, through miniaturizing the prep system (with narrow bore) or cryo-focusing the sample. This would increase the size of the ion beam, dramatically reducing the error attributed to low ion counts.

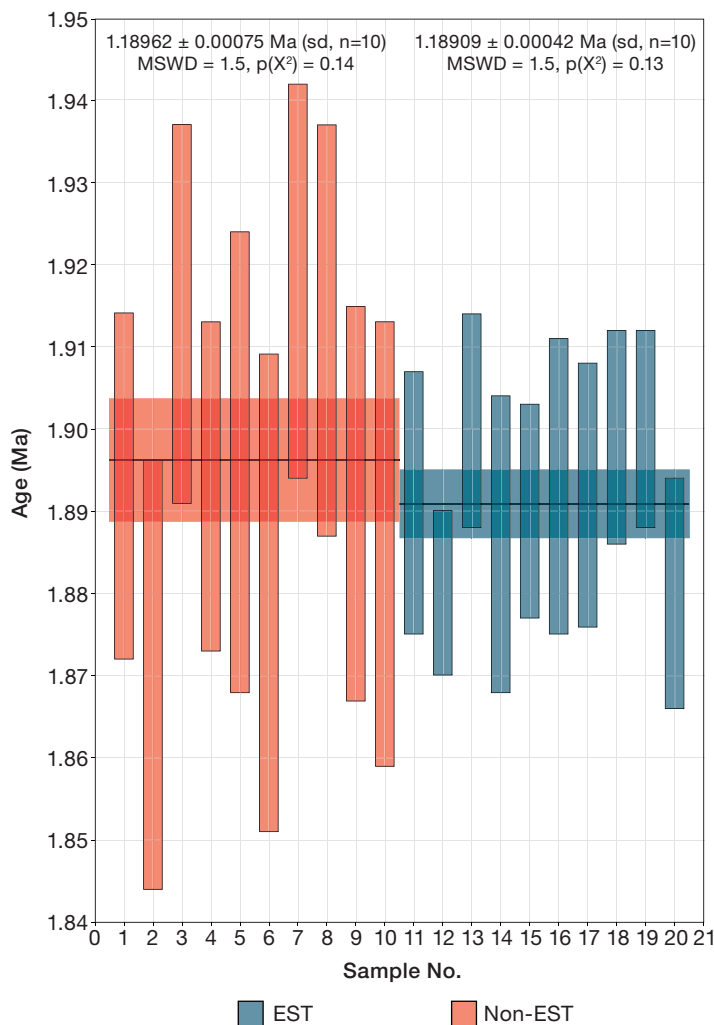


Figure 6. Effect of EST on the precision of Ar-Ar dates from Alder Creek samples. Traditional NG-MS (red) and EST (blue). With EST the sample sizes can be halved relative to traditional NG-MS and still achieve comparable levels of precision.

The future of NG-MS with EST

EST allows a greater degree of flexibility of analytical methods and prep designs. By switching off sample consumption during the “dark phase”, it is possible to extend methods with within-sample calibrations and detector switching, and longer equilibration times, without detriment to the overall accuracy and precision of the isotope measurement.

EST provides flexibility during method development. In cases where sample amounts vary from sample to sample, it is often helpful to be able to get a quick snapshot of the ion beam and to switch between ion counters or Faraday detectors depending on the size of the ion beam. EST makes this possible without losing valuable sample during the detector switching.

On-peak baselines provide information about the detector noise. With traditional NG analysis, on-peak baselines must be performed before or after the sample measurement. However, with EST, it is possible to go into ‘dark mode’ during sample measurement to perform on-peak baselines. This allows multiple measurements of detector noise during the sample analysis.

Perhaps the most significant implication of EST is the potential impact that it could have on beam intensities for a given sample size. Because EST enables equilibration times to be as long as necessary without impacting precision or accuracy of the isotope ratio, it is possible to dramatically increase signal sensitivity by decreasing the volume of the prep system or cryo-focusing sample before inletting into the MS. By using smaller diameter bore within the prep system, the overall volume of the system could be dramatically decreased resulting in less sample dilution through the prep and NG-MS system. Alternatively, cryo-focusing could be employed to collect the sample before introduction into the mass spectrometer. This means that for the same original sample size, the beam intensities would be greater. Such developments have the potential to open new research avenues using increasingly smaller sample sizes.

We have demonstrated the impacts of EST for argon isotopic measurements, but the benefits on other noble gas measurements are likely to be even more pronounced. The minor isotope of neon ^{22}Ne isobarically interferes with CO_2^{2+} . CO_2 inevitably enters the gas lines when opening the high-pressure valve to allow neon into the mass spectrometer from the prep system. Conventionally, users must wait until CO_2 is pumped down before starting the data acquisition for Ne. This results in valuable sample being consumed before analysis. However, with EST, it is possible to put the instrument into dark mode whilst the CO_2 is being removed, thereby maximizing the Ne ions counted.

For heavier isotopes, Kr and Xe, the equilibration times of the isotopic systems are much slower than for Ar. Therefore, there is a trade-off between waiting for isotopic equilibration and minimizing sample loss. With EST, this trade-off is removed. Samples can be equilibrated for as long as required without an effect on precision.

Summary

EST is a novel technology developed for the Thermo Scientific Argus VI noble gas mass spectrometer. It allows ionization to be switched off preventing sample consumption during the equilibration phase. This means that isotope measurements can be made at t0, allowing the original isotope ratio to be measured rather than extrapolated.

With EST, equilibration times can be as long as necessary without compromising precision or accuracy. We demonstrate that EST can, as a conservative estimate, improve Ar-Ar dating precision by >40% relative to non-EST methods. Furthermore, EST allows for more flexible methods, enabling within measurement baselines and detector switching without losing valuable sample. This technology opens the doors to small volume, long equilibration time prep systems, providing higher sensitivity for smaller sample sizes.

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