

Differentiating and Quantitative Analysis of N₂ and CO in the Presence of Each Other with a Quadrupole Mass Spectrometer

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Introduction

Due to the close proximity in the exact masses of N₂ (monoisotope exact mass 28.0056) and CO (monoisotope exact mass 27.9944), their separation and differentiation have been used to illustrate the resolving power of higher resolution MS systems. At unit mass resolution, both N₂ and CO would typically be measured within 28.0±0.2 Da, making it difficult if not impossible to tell whether the measured signal comes from one or the other or both. This paper will present a new MS calibration process which leads to the simultaneous quantitation of N₂ and CO on a conventional quadrupole MS with its ease of use, lower cost, and smaller footprint, ideally suited for industrial applications such as biofuel processing.

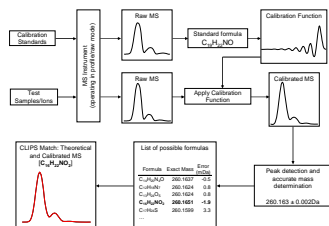
Methods

While it is sometimes possible to move to MS systems of higher and higher resolving power to separate overlapping mass spectral signals, a different approach will be presented in this paper to mathematically resolve these closely located and mutually interfering MS signals. To accurately deconvolute these overlapping signals, a unique mass spectral calibration has to be performed that calibrates not only m/z axis but, more importantly, mass spectral peak shape. With the Spectral Accuracy (Ref 1) achieved through this calibration, the overlapping mass spectral signals can now be resolved reliably and mathematically, leading to both qualitative (e.g., elemental compositions) and quantitative results (e.g., the relative concentration of the overlapping ions), even at unit mass resolution. As expected, larger and larger errors will be encountered as the overlapping signals become more and more closer to each other (collinearity), requiring higher and higher S/N to achieve a given level of RSD%. This paper will explore such dependence through both computer simulation and actual measurements on an Agilent GC/MSD system.

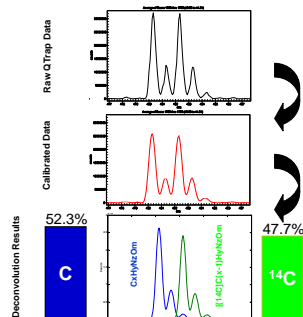
Theory

Unlike the conventional MS calibration, a novel calibration involving both m/z and MS peak shape allows for exact isotopic modeling and formula determination on even a unit mass resolution system, provided that the mass spectral signal is free from significant interferences arising from coexisting ions.

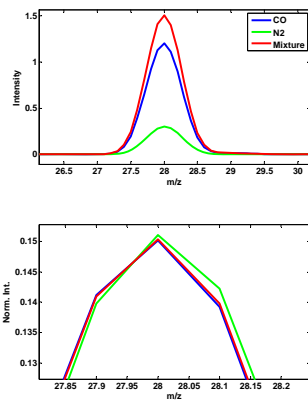
MassWorks CLIPS Formula ID



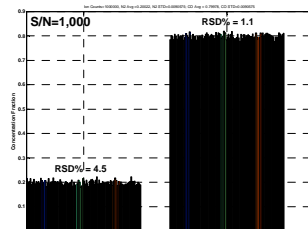
► In the presence of mass spectral interferences, the Spectral Accuracy and formula ID will be compromised.
 ► When the mass spectral interference is from an ion related to the ion of interest or another ion of known elemental composition, however, the same exact isotopic modeling can be expanded to include the interference ions in the Spectral Accuracy and formula ID process, as shown by the radio-labeling example below (Ref 2).



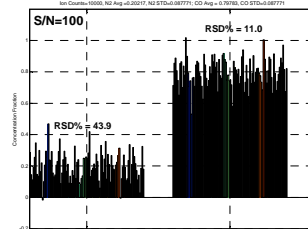
► With ¹⁴C radio labeling, the degree of overlap is fairly limited and the deconvolution is relatively easy. The deconvolution of N₂ and CO becomes quite a challenge due to the close proximity of their respective theoretical mass spectral responses at unit mass resolution, shown below.



Results and Discussion

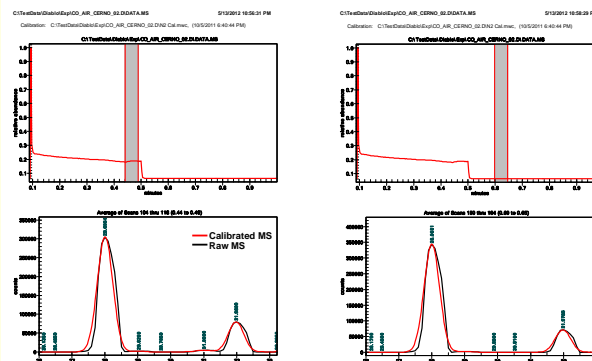


A computer simulation was first carried out to assess the technical feasibility of N₂/CO measurement with a single quad MS system at unit mass resolution. At 1,000,000 actual ion counts (or 1,000:1 effective signal to noise ratio), a 0.20:0.80 mixture of N₂/CO can indeed be accurately measured, with RSD at 4.5% and 1.1%, respectively, as shown on the left.

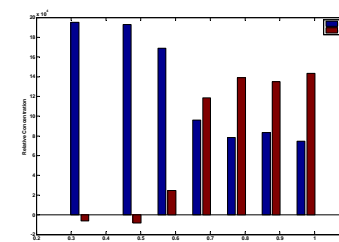


With 10,000 ion counts or 100:1 signal to noise ratio, as shown on the left, with RSD at 43.9% and 11.0%, respectively. This level of measurement accuracy for the lesser component (N₂ in this case) would not be acceptable for real applications. It is expected, however, that the actual signal to noise ratio would fall somewhere between 100:1 to 1,000:1, making it feasible to determine N₂/CO fractions with RSD=10% or less.

A experiment on Agilent GC/MSD with fittings and accessories for gas monitoring application was conducted where a mixture of N₂/CO was introduced into the MS system at 0.5min. It is expected that as the mixture enters into the system, the CO fraction would gradually increase, leading to an apparent accurate mass decrease from N₂'s 28.005 (below left, before mixture introduction) towards CO's 27.995 (below right, after mixture introduction), which was indeed observed during the experiment. The MS calibration was performed using the nearby O₂ peak.



3-sec MS scans are averaged from different portions of the whole 1-min experiment to test the feasibility for actual quantitative analysis of N₂ and CO, with the relative concentrations plotted out as a function of time in the graph below. The gradual increase of CO fraction and the gradual decrease of N₂ fraction can be clearly observed, consistent with the gradual diffusion process during the sample introduction and the downward accurate mass shift observed.



Conclusions

► Though very preliminary in nature, the determination of N₂ and CO in the presence of each other with a single quadrupole MS system seems to be feasible.

► Due to the close proximity of these two components, a signal to noise ratio of more than 100:1 and preferably near 1,000:1 is needed for accurate determination of both components to within less than 10% RSD.

► This requirement on signal to noise can be met with relative ease during real experimentation.

► It would be useful to establish a lower limit of detection with practically useful sampling time (e.g., 30 sec), which would be a subject of future research and experimentation.

► Another gas of practical application interest, C₂H₄, which is also nominally located at 28Da, may be included using the same mixture analysis approach to achieve the simultaneous quantitation of N₂, CO, and C₂H₄. This would also be the subject of a future research and experimentation.

References

1. Wang, Y., Gu, M. *Anal. Chem.* **2010**, *82*, 7055.
2. Wang, Y., Gu, M. *Proc. 57th ASMS Conference on Mass Spectrometry and Allied Topics*, Philadelphia, PA, May 31-June 4, **2009**.