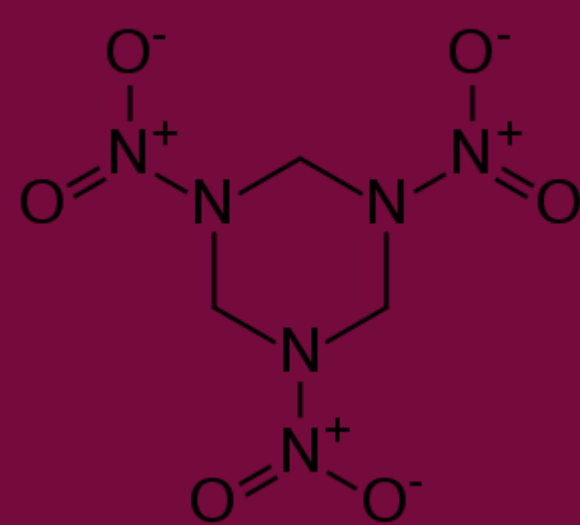
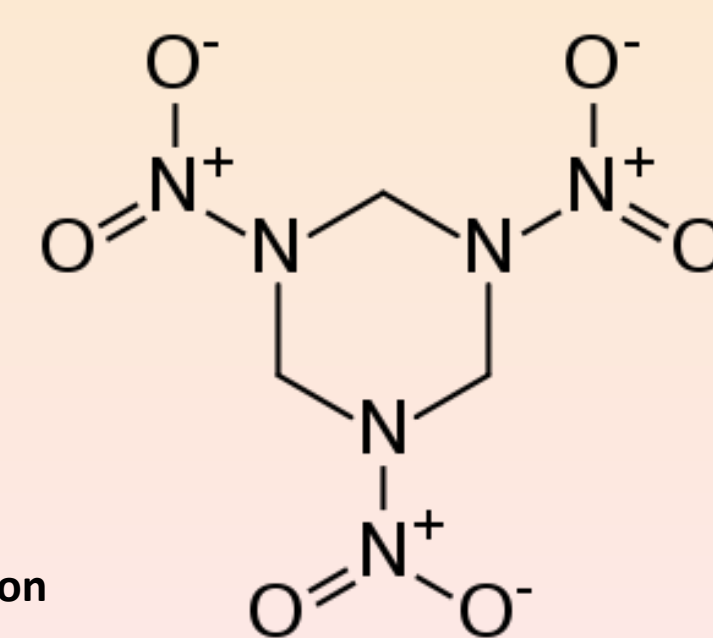


GC-IRMS Method for Measuring Carbon and Nitrogen Isotope Ratios of RDX



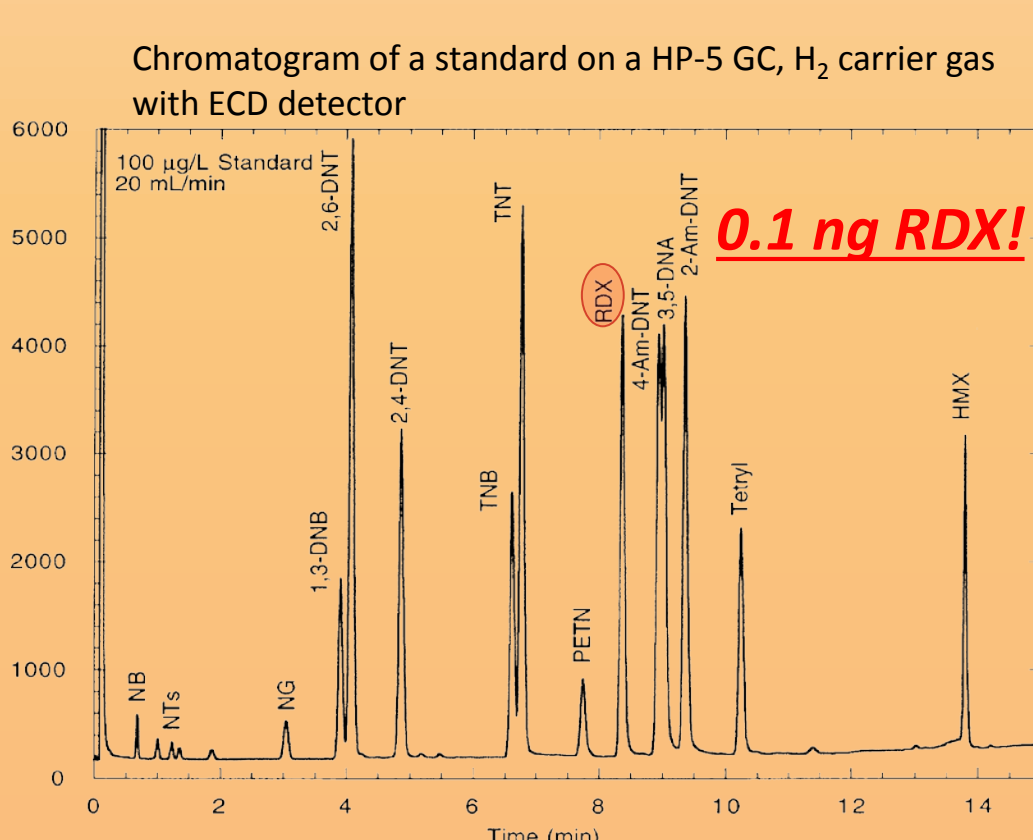
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Background

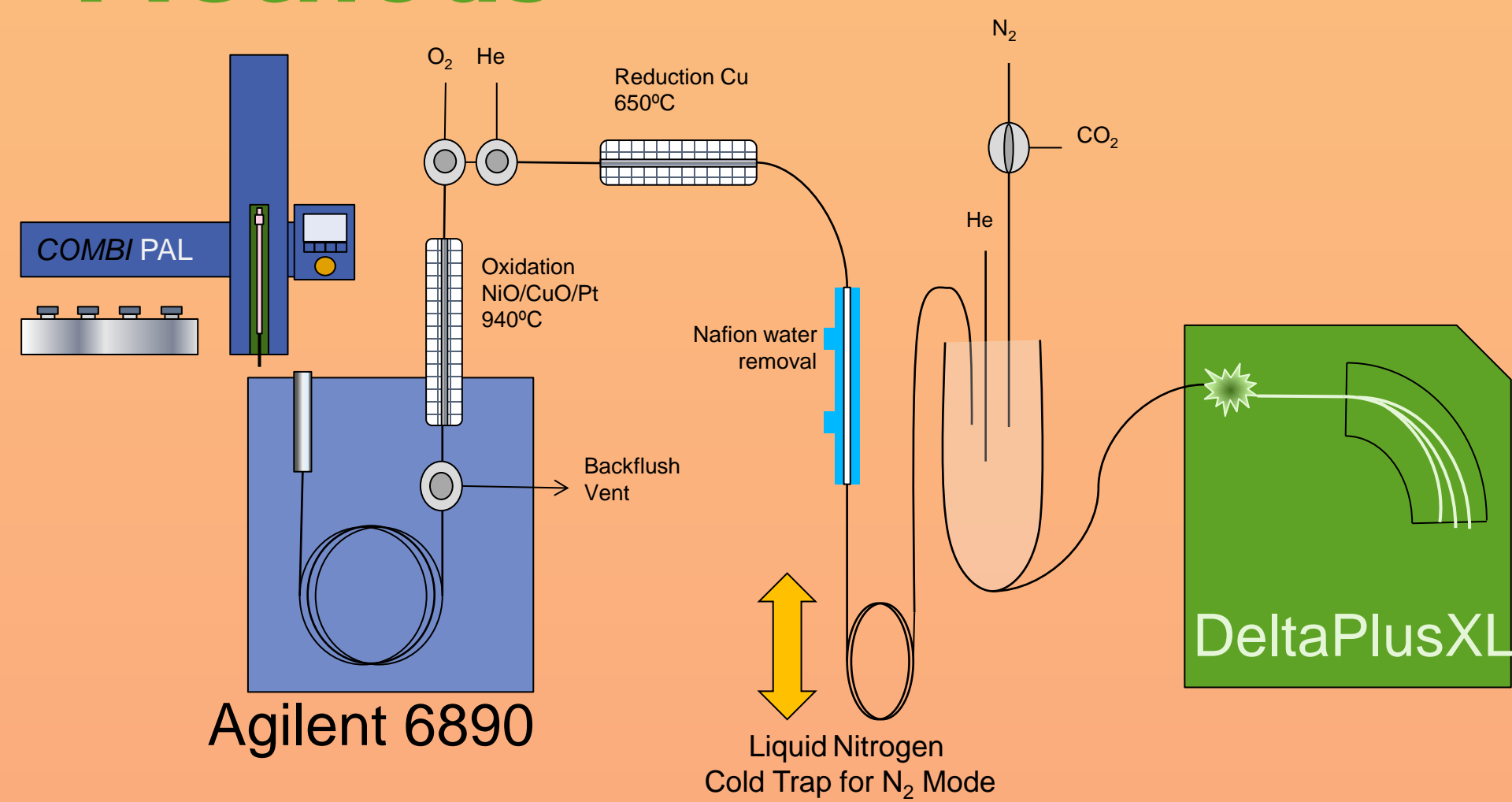
As a contributor to a DOE-SERDP funded project to combine state-of-the art analytical techniques, molecular approaches, and biogeochemical studies to enhance understanding of the biodegradation of the nitramine explosive hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) in subsurface environments the **Environmental Isotope Geochemistry Laboratory** at UIC has endeavored to measure isotope ratios of carbon and nitrogen in RDX.

An understanding of biodegradation and other processes will provide the Department of Defense with an enhanced ability to predict the fate of nitramines in contaminated groundwater environments and to more consistently enhance their rates and extents of biodegradation through active remedial approaches.



RDX is measurable by gas chromatography and EPA method 8095 EXPLOSIVES BY GAS CHROMATOGRAPHY was our starting point. However the method does not translate well to GC-IRMS; the amount of material measured by GC with an ECD detector is much too small to be seen by IRMS. Scaling up the method for continuous flow IRMS has presented multiple challenges

Methods



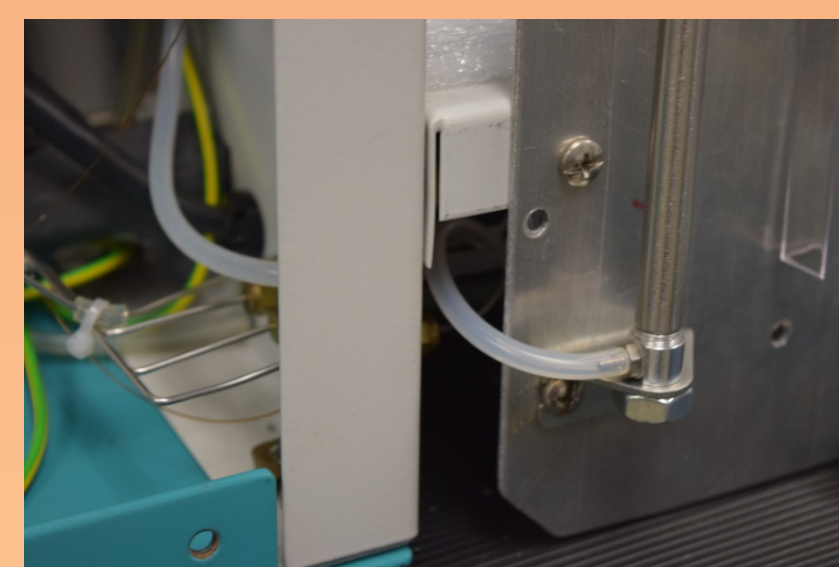
This work was performed using a Thermo Finnigan DeltaPlusXL interfaced to an Agilent 6890 GC with CombiPAL autosampler. One small modification of the GC-C III interface was made for nitrogen isotope measurement. No additional control solenoids or ISODAT scripts were required.



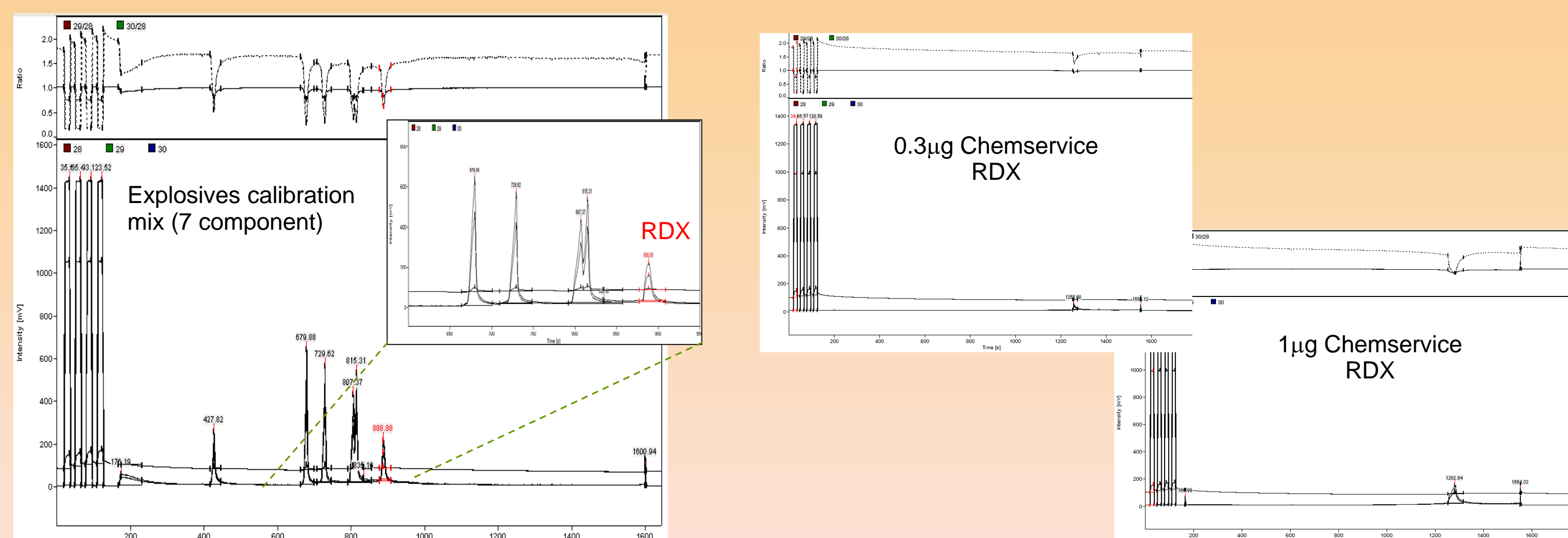
A linearly actuated pneumatic piston (BIMBA Manufacturing, University Park, IL) with a 6" draw was spliced into the same air line that actuates the open split sample injection. When the open split is "IN" a loop of the capillary transfer line from Nafion water trap to the open split is simultaneously lowered into liquid nitrogen trapping CO₂ thereby reducing formation of CO in the source which would interfere with N₂ measurement.



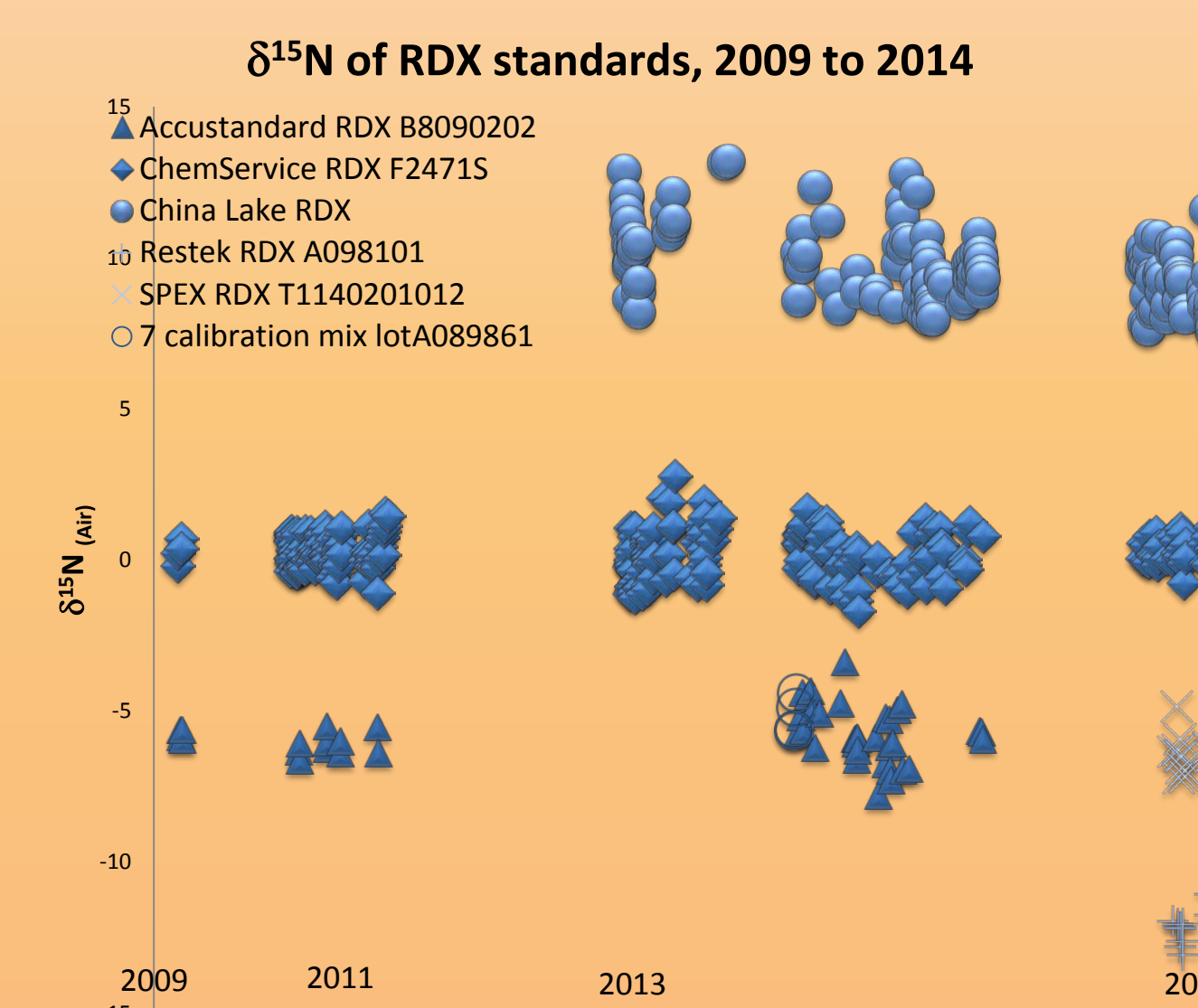
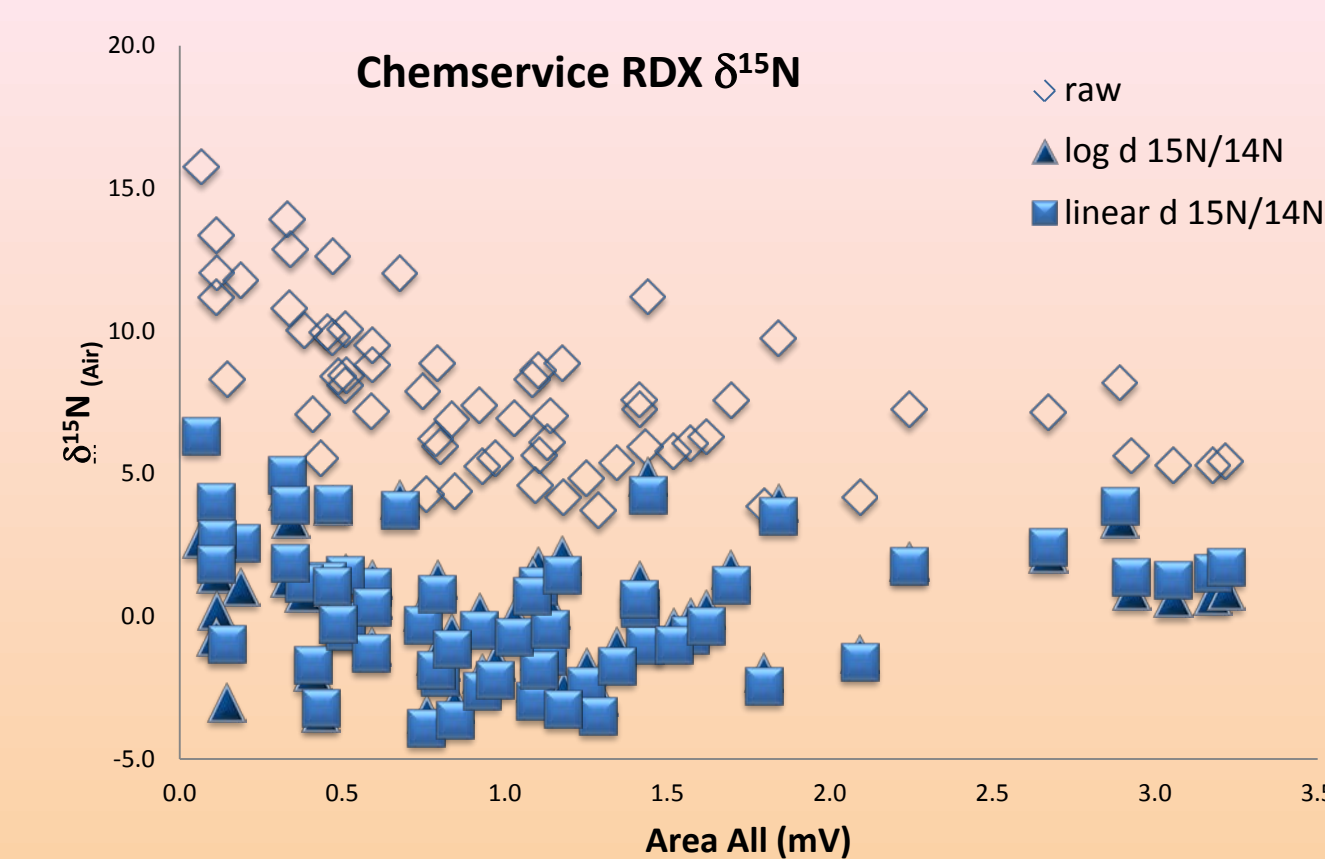
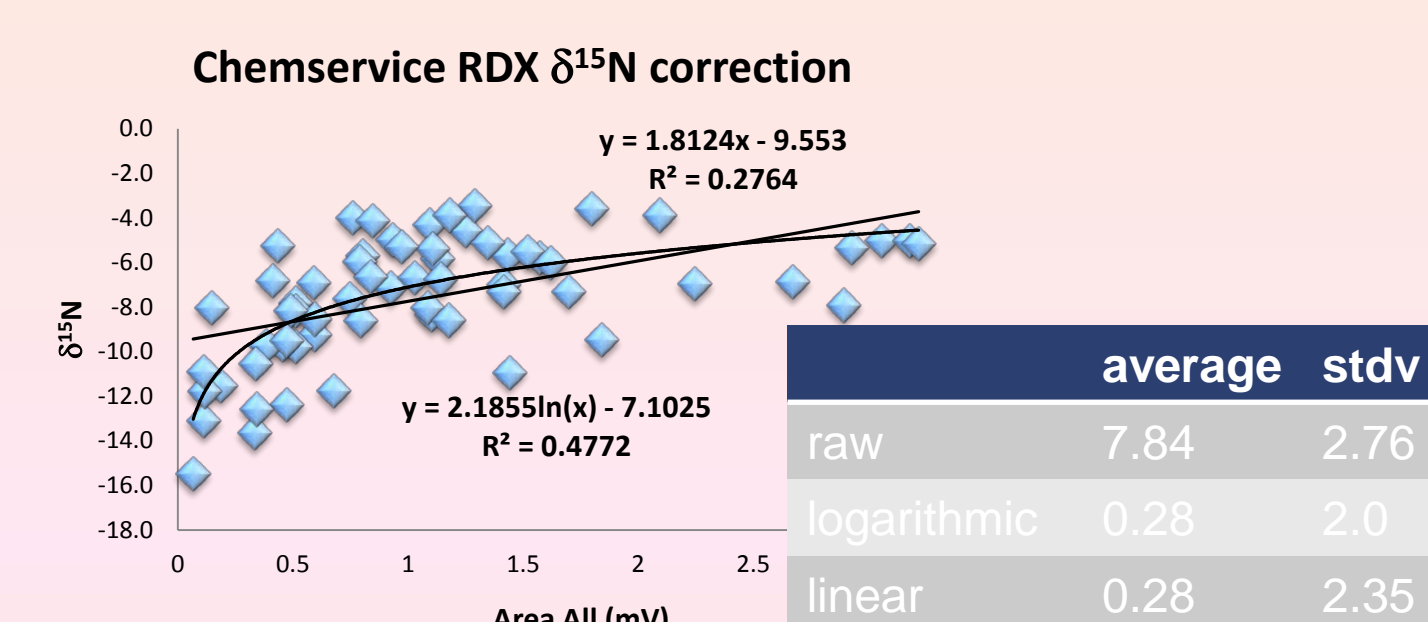
"Finnigan Hack" Note the appropriate use of wire bread bag ties!



For simple solutions, just RDX in acetonitrile, injections of 1-5µg produce measureable but very small peaks (~100mV) in the range that is usually discarded in GC-IRMS work. The relation between delta and peak area is not linear in this range. A logarithmic fit and data correction was used to squeeze meaning out of very small peaks.



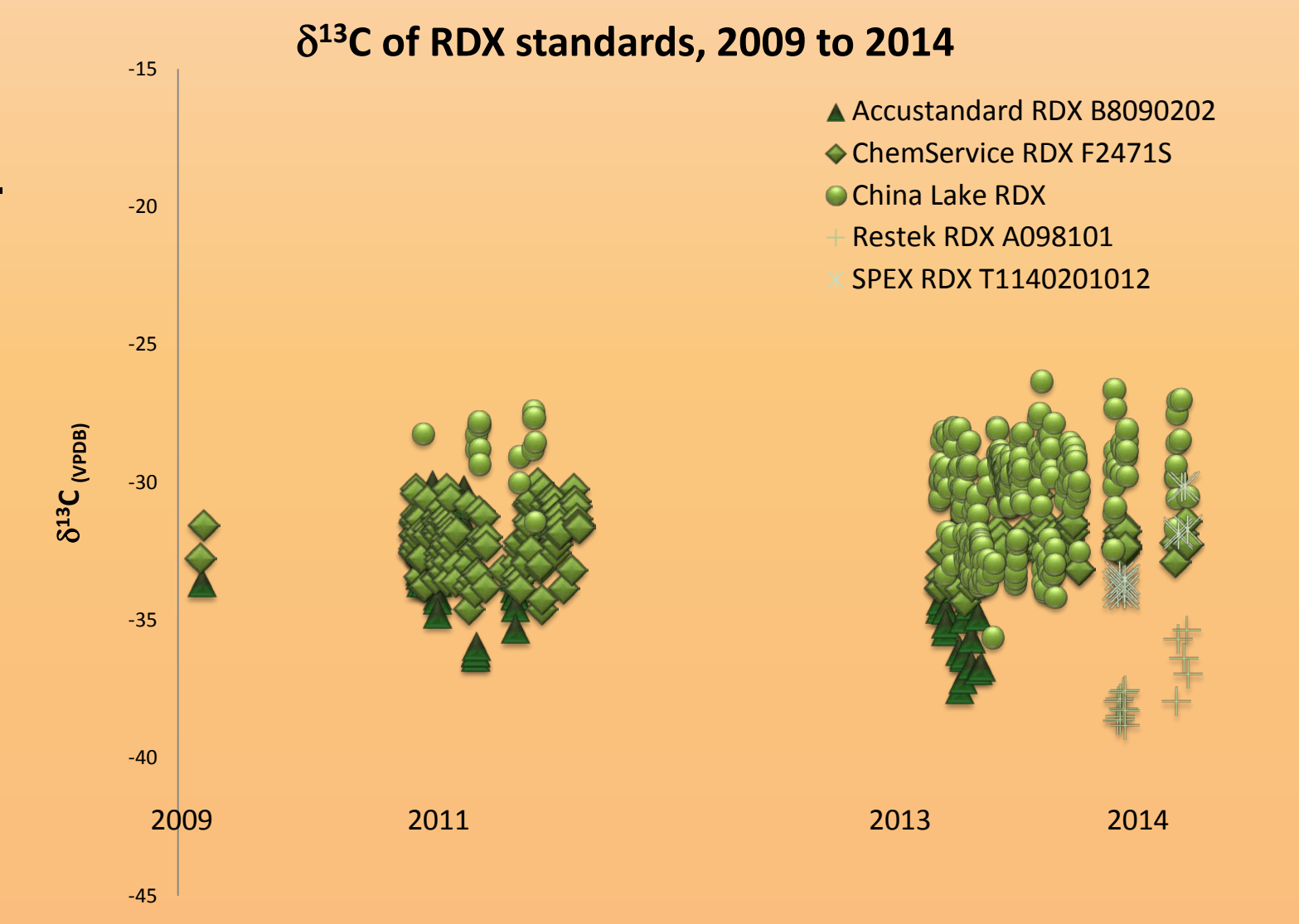
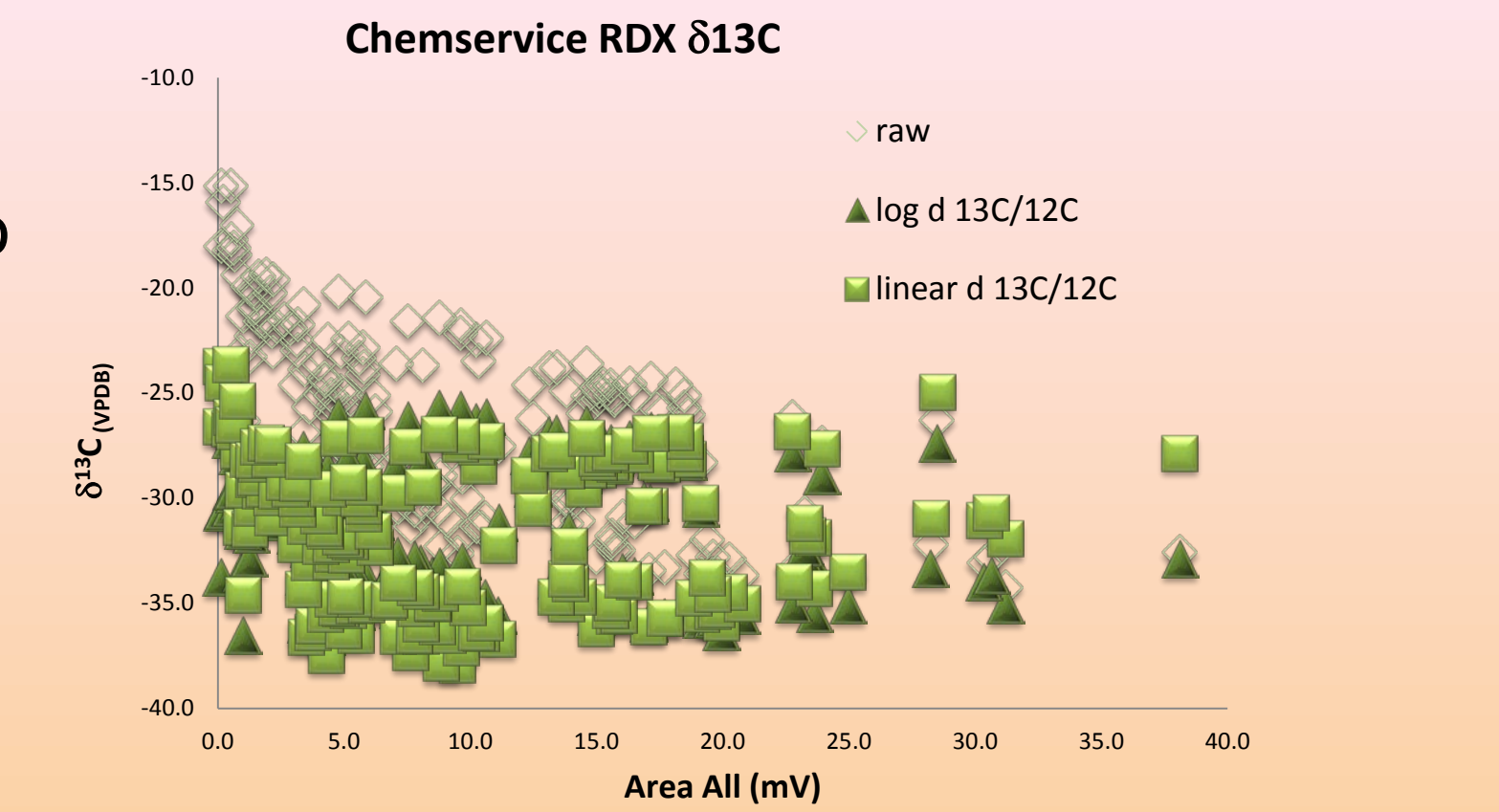
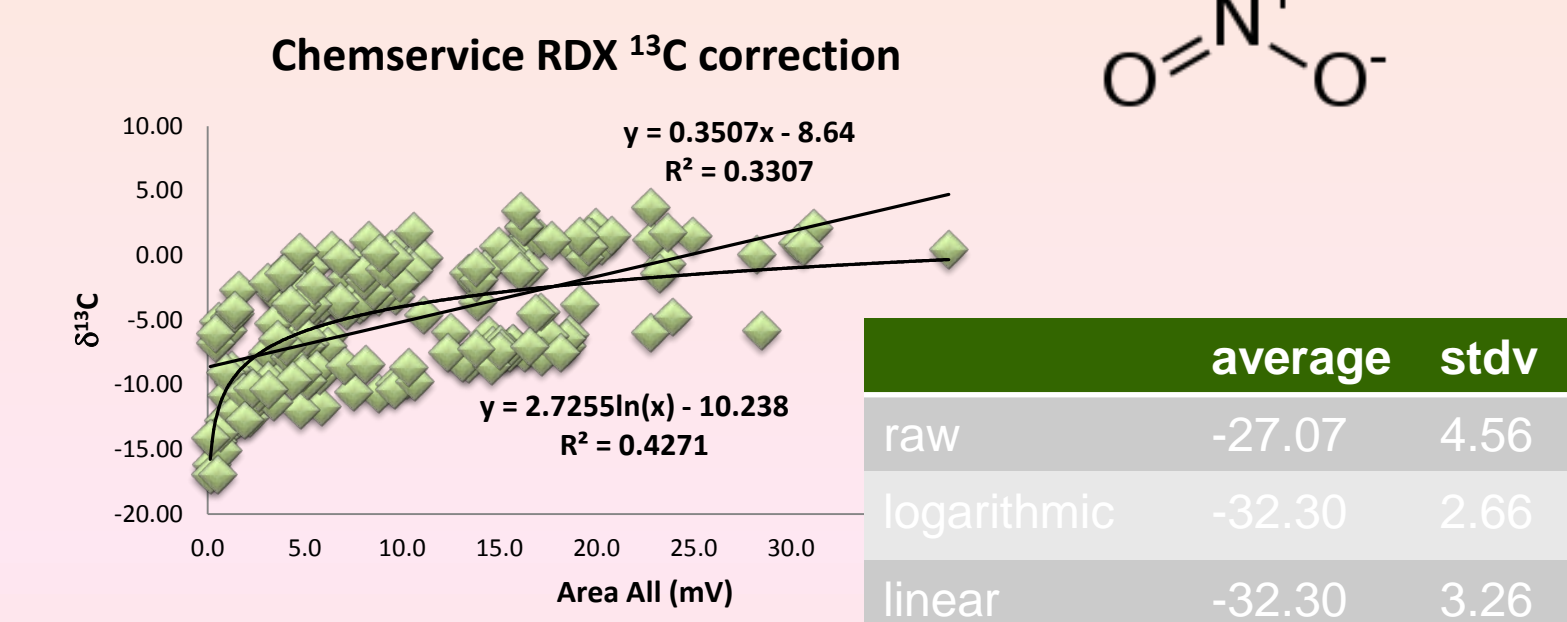
Results



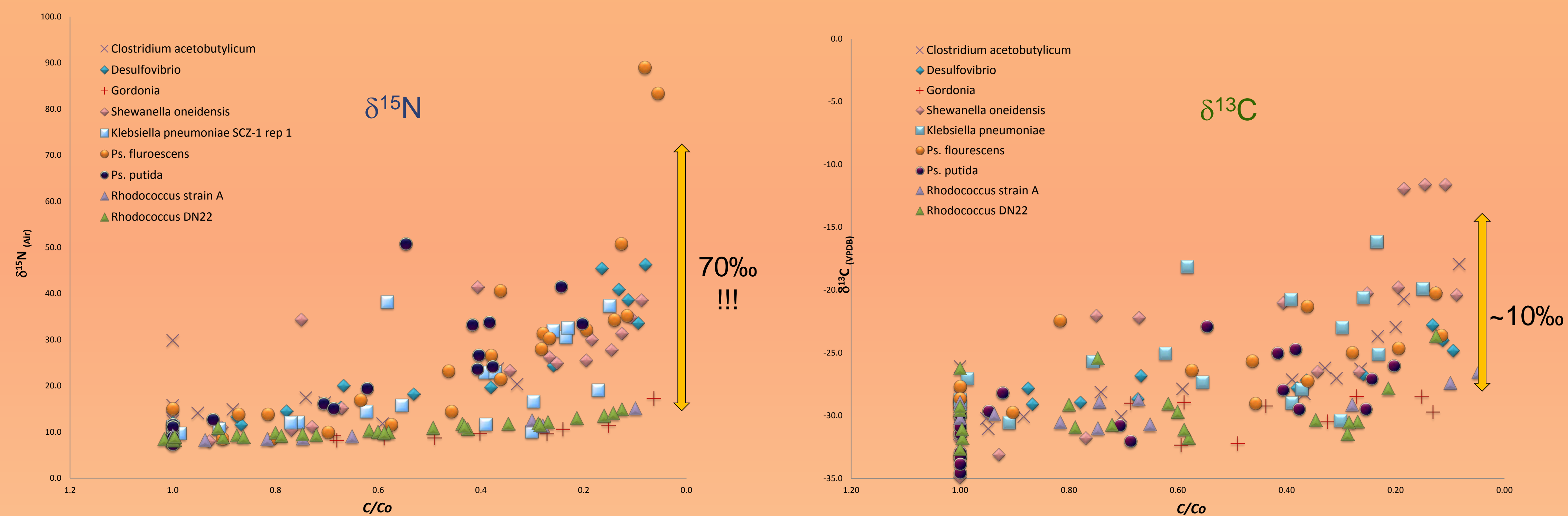
Isotope ratio values were assigned to two commercial RDX standards (Chemservice and Accustandard) by evaporating aliquots of each into tin capsules and analyzing by EA-IRMS against USGS-40 and USGS-41 (L-glutamic acid). These two standards were then used to calibrate a quality control sample ("China Lake") and also used for size corrections and data normalization.

Data correction performed by plotting a correction vs area all for multiple injections of a single standard. The best fit linear or logarithmic regression line was then used to calculate a correction for each analysis in the same batch as a function of peak area.

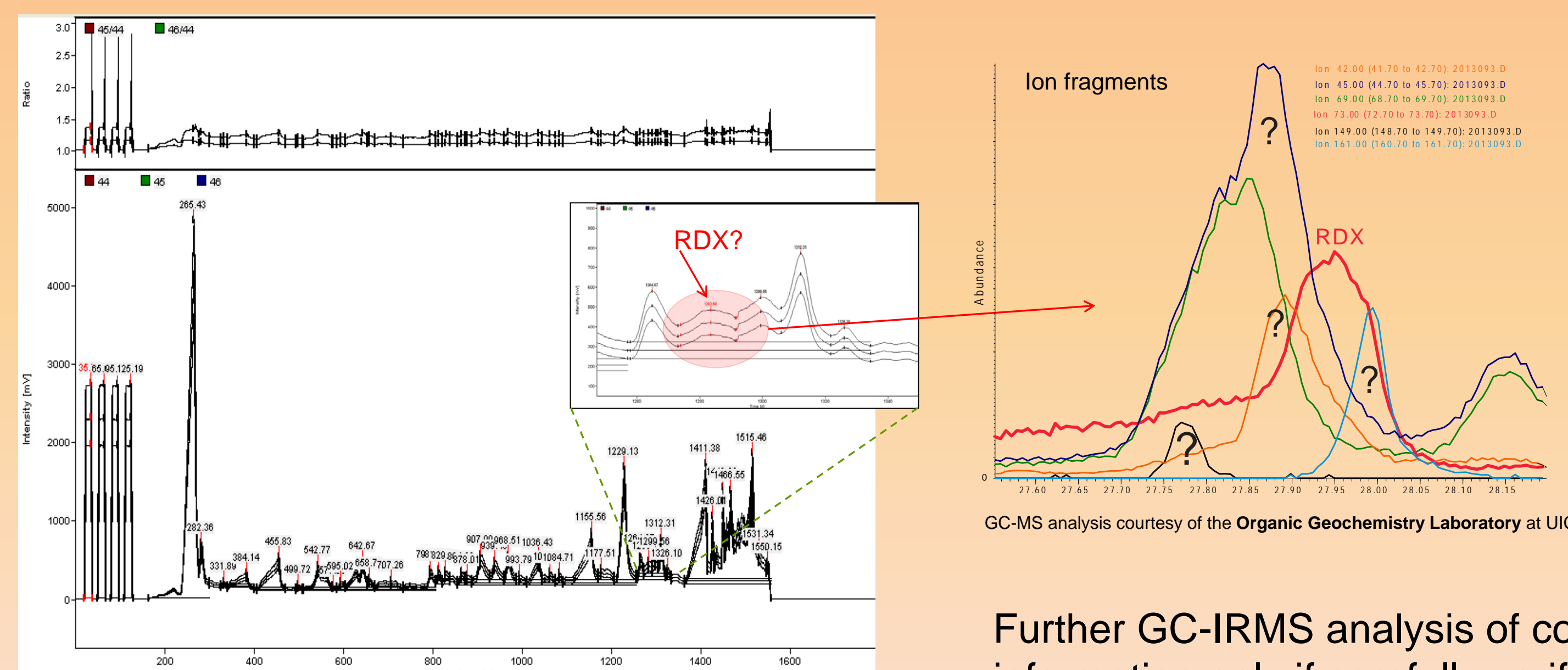
For IRMS analysis all samples and standards were diluted to the same concentration of RDX in acetonitrile. Thus the conditions within the GC inlet were comparable for each injection, normalizing any fractionation bias during the initial transfer of RDX from the vapor cloud to the column head.



RDX from batch culture experiments were extracted from solution by SPE processing. Samples (40 mL to 250 mL) were removed over the course of incubation, representing fractional RDX degradation in the range of approximately 0.05 to 0.95. Larger samples were filtered through GMF filters (25mm x 0.45µm pore size) to remove cells. The cleared sample was then passed over a pre-conditioned SupelcleanT ENVI-Chrom P solid phase extraction column (250 mg packing; Sigma-Aldrich, St. Louis, MO, USA). The analytes on the SPE column were eluted with acetonitrile according to the manufacturers instructions, and the extract was dried to a volume of 1ml. Final RDX concentrations were determined using HPLC.



Work has also begun on extracts from field samples (groundwater). A few of these samples are challenging the abilities of our current set-up. Co-elution of RDX with other unknown compounds in these complex mixtures is proving measurement of meaningful isotope ratios to be difficult. An example of one particularly complex sample is shown as a worst case.



Conclusion

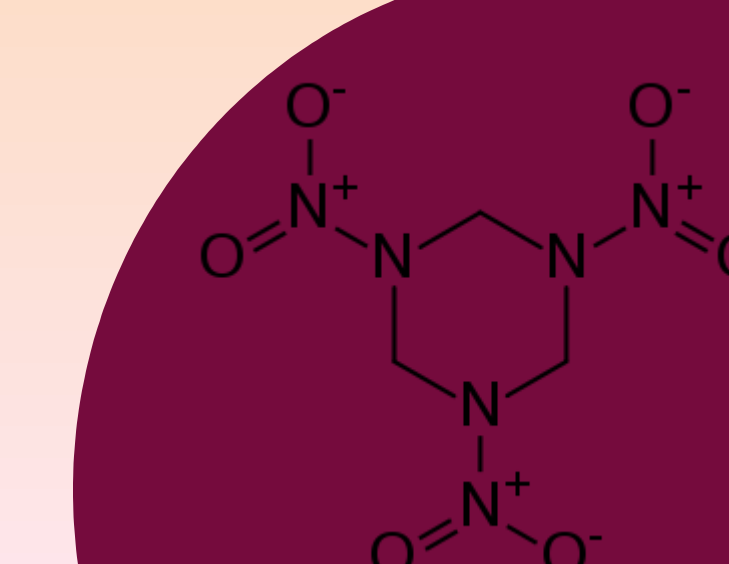
So with careful scrutiny we can extract meaningful isotope ratios from RDX in solution. Small peaks and ugly chromatography yield large standard deviations, however these uncertainties are small relative to the very large fractionations observed during anaerobic biodegradation (particularly in δ15N).

Further GC-IRMS analysis of complex field samples will yield meaningful information only if carefully verified by other methods (GC-MS). Additionally the importance of analyzing multiple standards is paramount.

References

METHOD 8095 EXPLOSIVES BY GAS CHROMATOGRAPHY Group Author(s): US EPA test methods for evaluating solid waste, physical/chemical methods SW-846 Published: 2007. US Government Printing Office (GPO), Washington, DC

Berg, J.B., J. Bolotin, and T. Hofstetter. 2007. Compound specific nitrogen and carbon isotope analysis of nitroaromatic compounds in aqueous samples using solid phase microextraction coupled to GC/IRMS. Analytical Chemistry, 79: 2386-2393



Acknowledgements

Roger Husted (Thermo Finnigan) for the idea to splice the open split air line! Fabien Kenig (UIC OGL) for GC-MS analysis and interpretation. Francesco Bellucci (UIC), Kyle Cronin (UIC), and Lionel Mojekwu (UIC) for thousands of injections pre PAL.