

THE HORIZON IRMS: SEQUENTIAL S, N AND C ISOTOPE ANALYSIS BY EA-IRMS

INTRODUCTION

The measurement of the nitrogen, carbon and sulphur isotope ratios of an organic sample within a single EA-IRMS analysis has over the years proved to be an appealing if not quite practical ambition. Issues exist such as the long retention time of SO₂ resulting in small and wide SO₂ peaks, limited NO_x reduction capacity, and the lack of effective tracking of the peak centres of each gas species which can drift due to changes in electromagnet temperature.

In collaboration with Hekatech GmbH (Wegberg, Germany) solutions to all these issues have been developed in a manner that provides fast SNC analysis (less than 11 minutes total analysis time), accurate and precise measurements (generally better than 0.1‰ precision on all species), and an EA-IRMS solution that is capable of analysing greater than 400 samples per reactor filling.



Instrumentation

The Horizon IRMS from Nu Instruments is designed for flexibility, reliability and high performance operation, with user friendly instrument control and data analysis software. This next generation instrument possesses unique features for Continuous Flow (CF) analysis, interfacing to a wide range of sample preparation peripherals. The analyser is differentially pumped and incorporates Nu Instruments unique patented zoom optic system.

EuroVector design, manufacture and sell elemental analysers for CHNS-O determination in a wide variety of applications. The EA3000 Series is the comprehensive answer to EA combustion and pyrolysis applications.

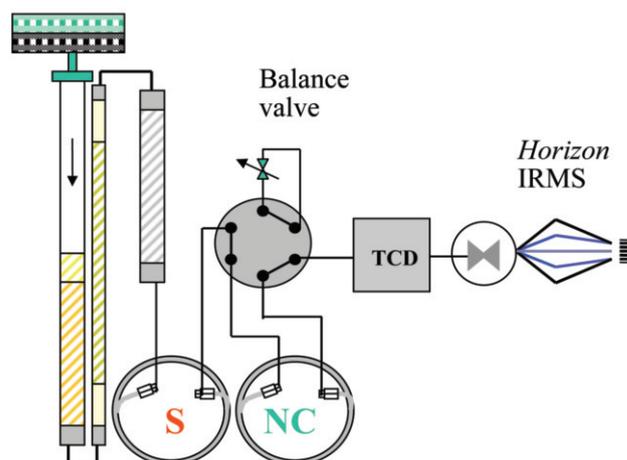
Experiment

A EuroVector EA 3024 elemental analyser was fitted with two GC columns (marked S and NC) operating in isothermal mode within the same EA oven (Figure 1). The oxidation reactor configuration consisted of the standard combustion / reduction tube packing for NCS analysis and was set to a temperature of 1030°C.

In addition, a second narrow bore tube packed with copper was located in the reduction furnace which was set to a temperature of 800°C. Finally, a magnesium perchlorate packed water trap was fitted.

Figure 1: Analytical setup

EuroVector EA



Discussion

The effluent from the first reactor flows through the sulphur column (S in the diagram, Figure 1) and on to the 6 port switching valve (Valco). This valve can either switch the flow to the nitrogen carbon (NC) column or else pass it directly to the TCD and IRMS via the flow resistance balance valve. The balance valve is needed so that there are constant flow conditions regardless of which path the flow is directed.

The combustion gases SO₂, N₂ and CO₂ exit the water trap and enter the sulphur column. The column switching valve is set so that gases eluting from the S column pass into the NC column. The speed of elution from the sulphur column is such that N₂ and CO₂ co-elute very quickly onto the NC column leaving SO₂ only on the sulphur column.

The column switching valve is then triggered and the flow in column S passes through the balance valve and on towards the IRMS leaving the N₂ and CO₂ trapped (zero flow) in the NC column. The SO₂ is then analysed for ³⁴S after which the IRMS peak jumps to nitrogen, the switching valve reverts back to the original configuration above, and the N₂ and CO₂ are now analysed as in a standard ¹⁵N and ¹³C measurement.

Figure 2: Salmon chromatogram

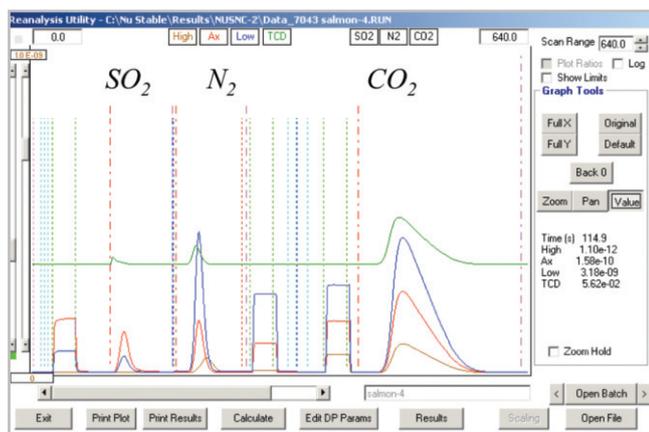
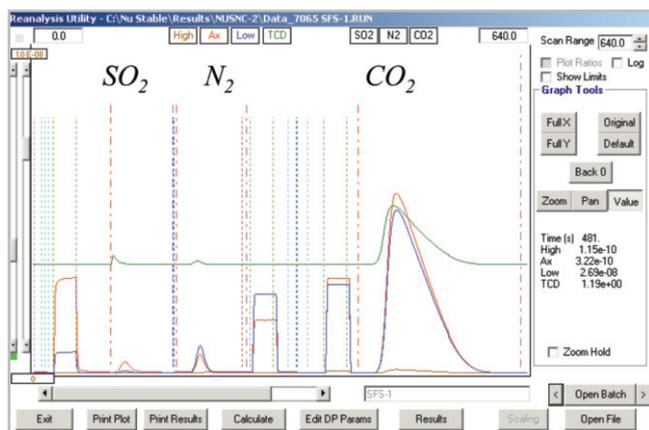


Figure 3: Wheat chromatogram



By applying the timings and order of analysis in this manner, the SO_2 is eluted first from a very short column (20cm). As a result peak broadening is reduced to a minimum whilst peak height is maximised. Both of these characteristics improve markedly the conditions for achieving good sulphur isotope measurements even for natural samples containing very small amounts of S. Figures 2 and 3 show typical chromatograms including the introduction of reference gas peaks. Automatic peak centring on all species is enabled and the Nu diverter is used to dilute the large quantities of CO_2 generated. This method of managing the analysis of N, C and S in a single analysis confers a number of advantages:

- By allowing SO_2 to elute first any peak broadening is minimised and peak height is maximised.
- The choice of columns reflect the needs of the individual species analysed. There is no compromise.
- The extension of the copper reduction phase by the use of a second reactor significantly increases the number of samples per reactor filling. At the time this data was obtained the reactor had already provided more than 200 analyses.
- The system is flexible, as demonstrated by Hekatech GmbH (Technical Note CHN007). The order of the analysis can be changed to, for example, to elute N_2 first, followed by SO_2 and CO_2 .

Conclusions

The technical innovations of the sample methodology described here allow three individual isotope measurements in less than eleven minutes from a single sample analysis. In combination with the stability, linearity and peak jumping capabilities of the Nu Instruments Horizon IRMS, the analytical performance reflects a method that is precise, sensitive and accurate. It offers higher throughput for less consumable costs. It provides the user with a no compromise solution that truly addresses a triple ^{34}S , ^{15}N and ^{13}C analysis on a natural organic sample.

The results shown in Table I show precisions typically better than 0.1‰ on all species and better than 0.15‰ on sulphur measurements on samples containing as little as $3\mu\text{g S}$.

Table I: Results obtained from analysis of a range of organic samples.

Sample	Weight mg	S μg	$\delta^{34}\text{S}$	σ_n	N μg	$\delta^{15}\text{N}$	σ_n	C μg	$\delta^{13}\text{C}$	σ_n	n
casein	0.2-2.2	1.5 -16	7.21	0.06	30-300	5.76	0.07	100-1000	-26.98	0.04	20
algaeS	2	18	7.51	0.09	210	5.12	0.21	940	-31.52	0.02	5
algaeB	1.2	34	19.13	0.15	15	8.22	0.19	410	-17.97	0.08	5
salmon	2	19	10.55	0.07	250	10.33	0.03	1030	-19.55	0.02	5
trout	2	25	15.2	0.02	295	11.44	0.01	910	-20.04	0.02	5
wfs	3.5	3	-1.59	0.14	50	2.98	0.01	1470	-27.00	0.01	5
sfs	3.5	3	9.43	0.13	52	1.67	0.06	1400	-13.68	0.06	5

Acknowledgements

Nu Instruments would like to thank Klaus Hecker of Hekatech GmbH for his kind assistance in reviving the two-column solution, which was key to the development of this analytical technique.