A Potentially Compounding Factor Affecting ^2H Isotope Analysis of Explosives by TC/EA-IRMS

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Background

Observations made in our lab when analysing CO_2 standards [5 vol% in argon] for ^{13}C-isotopic abundance, suggested an interference between the two gases whereby molecules of the interfering gas [argon] competed with the target gas [CO_2] for ionisation. In the absence of an alternative, we termed this affect 'ionisation quench' or 'IQ'. Here we set out to investigate whether such an IQ-effect would occur (and if so, to what extent) when measuring a compound of known ^2H-isotopic composition [IAEA-CH7; δ^2H_{VSMOW} -100.3 ‰] in the presence of nitrogen. We have further identified a maximum 'safe' nitrogen-content threshold above which accuracy of ^2H-measurement under "standard" operating conditions becomes doubtful.

Any impact on the ability to accurately measure ^2H-isotopic abundance of nitrogen-rich compounds would have to be taken into account when analysing a variety of compounds although of interest to us would be highly energetic materials such as ammonium nitrate, RDX and the RDX precursor hexamine.

Methodology

Approximately 0.1 mg of the international reference material (IRM) IAEA-CH7 (polyethylene) samples were weighed into silver caps to which increasing amounts of $AgNO_3$ (chosen as controllable source of nitrogen) were added [range approx 0.1 mg-0.75 mg]. Prior to analysis, samples were stored in an evacuated dessicator over phosphorus pentoxide for 7 days. Samples were also prepared containing IAEA-CH7 only [approx 0.1 mg] and $AgNO_3$ only, both treated as described for IAEA-CH7 plus $AgNO_3$.

Samples were introduced into a Thermo-Finnigan Delta^{plus}XP coupled to a high temperature conversion elemental analyser [TC/EA] by means of a Costech zero-blank autosampler (reactor temp. 1425°C, post-reactor GC-column [5Å molecular sieve] temp. 85°C, carrier gas flow approx. 90 ml/min). Hydrogen and carbon monoxide ref gases were set to 1.0 and 1.45 bar respectively. Measured $^2H/^1H$ isotope ratios are expressed as δ-values [‰] relative to VSMOV..

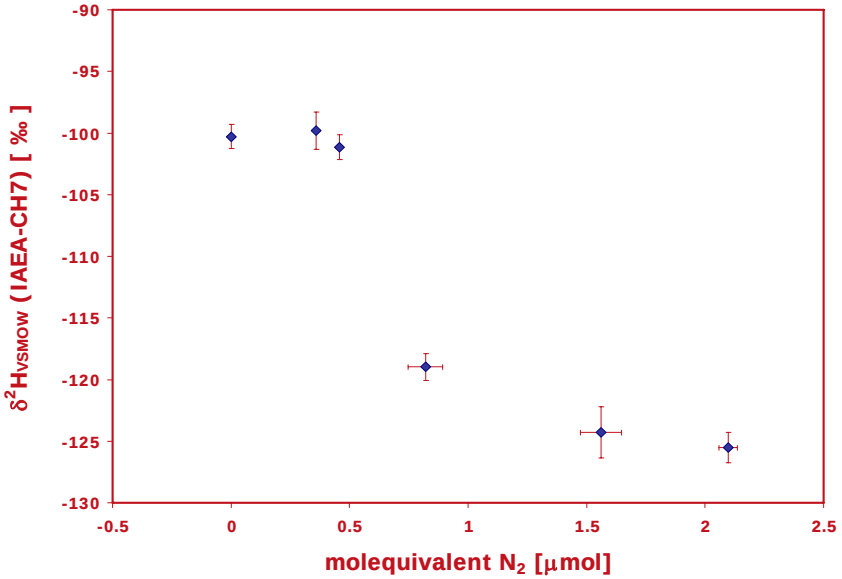

Fig. 1: Influence of increasing amounts of N_2 concurrently present in the sample on measured δ^2H-values of IAEA-CH7.

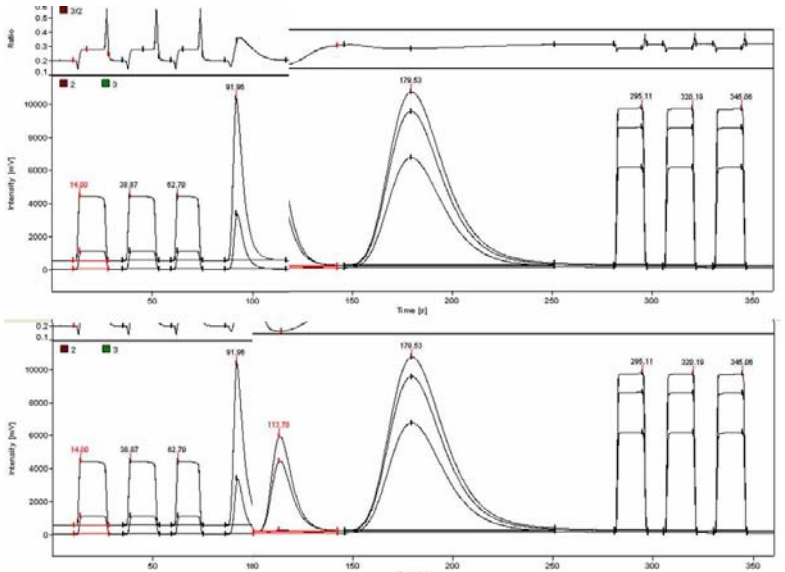

Fig. 2: Overlay of two separately run TC/EA analyses of IAEA-CH7 and $AgNO_3$ demonstrating the extent of peak overlap between H_2 and N_2 at 85°C (GC).

Results and Discussion

A relationship between measured δ^2H-values and amount of nitrogen present in combined samples (containing both IAEA-CH7 and $AgNO_3$) was observed resulting in loss of accuracy for the accepted δ^2H-values of IAEA-CH7 (Fig. 1) and a 20 – 25% loss in both H_2 peak height and peak area under "standard" operating conditions, i.e. GC temp. of 85°C.

Analysing a nitrogen-rich sample at a GC temp. of 85°C results in a peak overlap of typically 18 s of the H_2 peak tail with the N_2 peak front (Fig. 2).

How little sample material will already impair accuracy of ^2H isotope analysis of nitrogen-rich compounds such as explosives and their precursors has been calculated on the basis of our model experiments and these results are presented in Table 1.

The effect of reduced GC temperature on N_2 retention time as a potentially remedial action is summarised in Table 2.

Table 1: N_2 Mol-equivalents for Nitrogen-Rich Compounds#

[µg] Sample	N_2 [µmol] $AgNO_3$	N_2 [µmol] NH_4NO_3	N_2 [µmol] TNT	N_2 [µmol] Hexamine	N_2 [µmol] RDX
0	0.00	0.00	0.00	0.00	0.00
122	0.36	1.53	0.85	1.94	1.65
155	0.46	1.94	1.08	2.46	2.09
278	0.82	3.48	1.94	4.41	3.76
530	1.56	6.63	3.70	8.41	7.16
713	2.10	8.91	4.97	11.32	9.64

The figures underlaid in yellow correspond to sample amounts that would negatively impact on accuracy of ^2H isotope analysis under "standard" operating conditions of GC @ 85°C and carrier gas @ ~90 ml/min.

Table 2: Effect of GC Temperature on N_2 Peak Retention

GC [°C]	Peak Start [s]	RT [s]	Peak Width [s]
30	119.0	140.25	58.0
50	110.6	128.0	51.0
60	107.5	123.25	47.25
85	100.7	113.7	42.2

Outlook

Based on these results two potential ways of remedial action warrant further investigation. (1) Run ^2H isotope analyses of explosives at a GC temp. of 30°C although this still requires a systematic study to demonstrate H_2 peak parameters are not adversely affected so as to compromise accuracy and precision of measured δ^2H-values even if there is no peak overlap with N_2. (2) Investigate the potential of using a different stationary phase for the GC column such as HaySep Q.