

Application report

High sensitivity $\delta^{34}\text{S}$ analyses in bone collagen

AB-I-211210-E-01

In archaeological research $\delta^{13}\text{C}$, $\delta^{15}\text{N}$ and $\delta^{34}\text{S}$ isotope ratios in bone collagen offer valuable insight for dietary reconstruction of prehistoric man, which furthers our understanding of early human migration patterns and their quest for survival. In this field of research it is essential that as much useful information as possible is derived from the limited sample amounts that are available. In this application report we will describe how Elementar's purge and trap technology coupled to the IsoPrime100 offers exceptional advantages for these difficult samples.

Simultaneous analysis of C, N and S isotopes is difficult due to the very high C:S ratio of bone collagen (C:S > 200:1), which can create problems with the gas separation required prior to isotopic analysis. This is no problem for elemental analysers of the *Elementar* vario cube series, since the patented "purge and trap" chromatography can reliably separate CNS peaks, even for extremely large element ratios apparent in natural samples. The temperature ramping also leads to very sharp peaks and hence improved signal-to-noise ratios, which enables analyses in the lower microgram range. Moreover, the increased dynamic range of the IsoPrime100 allows the analysis of samples over a large concentration range.



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Method

Bone collagen samples were analysed with the IsoPrime100 isotope ratio mass spectrometer coupled to a vario MICRO cube elemental analyser (EA-IRMS). The peak separation of the post-combustion products N_2 , CO_2 and SO_2 are shown in Figure 1. Since the purge and trap technique is used throughout the *Elementar* vario cube series, this high performance separation is observed with all elemental analysers of the vario cube series.

The vario MICRO cube is run in CNS mode with a combustion temperature of 1150°C . After sample combustion, CO_2 and SO_2 are trapped on a temperature programmable desorption (TPD) column, whilst N_2 passes through the column without being trapped. Once the N_2 peak has decayed back to baseline, the TPD is automatically heated to 90°C to release CO_2 and subsequently to 220°C to release the SO_2 . Each heating step takes place only after completion of the subsequent peak detection by the elemental analyser, guaranteeing a complete baseline peak separation even for large relative concentration differences. Each separated combustion gas is then directed to the IsoPrime100 IRMS for isotope analysis (see Figure 1). Only the CO_2 peak was diluted 10x with Helium before entering the IRMS.

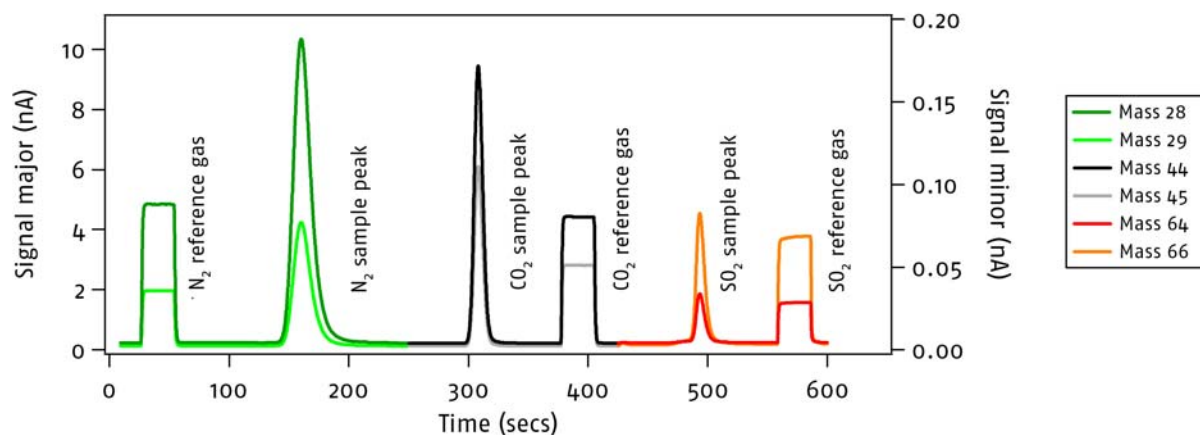


Figure 1. N_2 , CO_2 and SO_2 signals of the IsoPrime100 IRMS. The temperature controlled desorption from the purge and trap column results in an excellent peak separation of N_2 , CO_2 and SO_2 , independent of the C:S ratio of the sample.



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Results

The performance of the vario MICRO cube – IsoPrime100 IRMS system for a bone collagen standard is summarised in the following table. For comparison, data of the same bone collagen standard analysed on an EA with a conventional 0.7m PTFE isothermal GC column coupled to the IsoPrime100 IRMS is also shown.

	GC column	Purge & Trap
Average collagen sample weight (mg)	3.97	1.95
Absolute sulphur weight in present sample (μg)	11.9	5.84
Average sample peak height (nA)	0.99	1.94
Instrument sensitivity ($\mu\text{g S/nA}$)	12.2	3.0
Ionisation trap current (μA)	800	400
Effective instrument sensitivity @ 400 μA trap current ($\mu\text{g S/nA}$)	24.4	3.0
Standard deviation of collagen samples (‰)	0.37	0.22

** The analyses were performed in cooperation with Dr. Fiona Petchy, University of Waikato, New Zealand.*

Taken into account the doubling of the trap current, the use of the purge and trap technique generates an 8x increase in SO_2 sensitivity. Moreover, a higher measurement precision was achieved by using the purge and trap technique.



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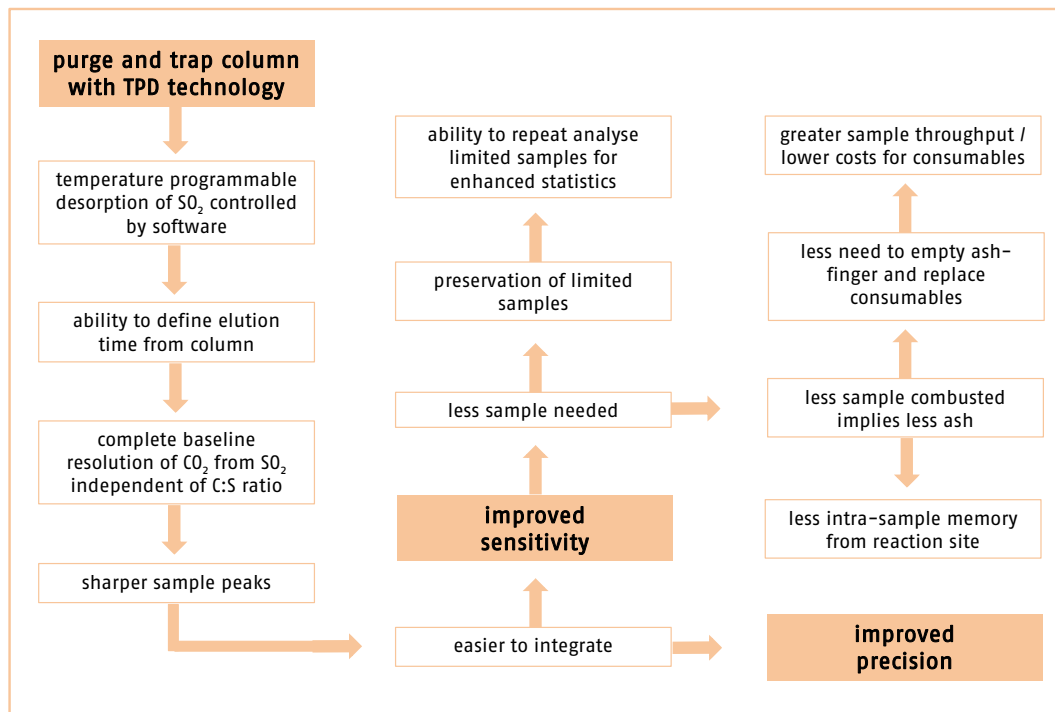
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Summary

The $\delta^{34}\text{S}$ ratio of bone collagen can be measured with a high precision using the vario MICRO cube – IsoPrime100 IRMS system, even at very low absolute sulphur contents (typically $< 5 \mu\text{g S}$). Compared to analyses using an elemental analyser with GC column, a better precision and sensitivity was achieved, even at a much lower trap current. Because of the excellent SO_2 chromatography a lower trap current can be used, which results in a more stable instrument and longer lifetime of the filament.

The higher sensitivity accomplished by the “purge and trap” technique allows analyses with lower sample weights, which is important when only low amounts of sample material are available. Additionally less ash will remain in the ash finger, allowing a greater sample throughput and less intra-sample memory from the reaction site and a reduction of the costs for consumables.



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