

(removing the ash) or changed after about 600 samples. The copper in the reduction reactor usually is oxidized after 200 samples and has to be reduced by flushing with hydrogen under heating. Each series of samples is controlled by regularly including measurements of a standard substance of known elemental as well as isotopic composition. Following combustion, reduction and water removal the gases are separated gaschromatographically (Porapak Q, 2 m). The concentration of the compounds is determined by a TCD (thermal conductivity detector). The retention times under the conditions of operation are 160 s for nitrogen and 275 s for carbon dioxide. A typical run is shown in Fig. 3. The TCD signals of nitrogen and carbon dioxide exhibit a ratio of about 1 : 25, which is typical for plant material. In the case shown the reference substance used is atropin. Table I demonstrates a typical example from a whole sequence run to illustrate the precision of the technique. The dummy samples preceding each run are not shown.

TABLE I. PART OF A TYPICAL RUN OF ATROPIN STANDARDS AND TWO IAEA-NITROGEN STANDARDS (RAW DATA).

Sample	δ ($^{13}\text{C}/^{12}\text{C}$) ‰ v.s. PDB	stand. deviation $^{13}\text{C}/^{12}\text{C}$	δ ($^{15}\text{N}/^{14}\text{N}$) ‰ v.s. air- N_2	stand. deviation $^{15}\text{N}/^{14}\text{N}$
Atropin	-3.9		-17.8	
Atropin	-3.9		-17.9	
Atropin	-4.1		-17.4	
Atropin	-3.8		-17.5	
Atropin	-3.9		-17.3	
Atropin	-4.0		-17.5	
Atropin	-3.8		-17.8	
Atropin	-3.9	0.1	-17.5	0.2
IAEA-N1			2.6	
IAEA-N1			2.5	
IAEA-N1			2.6	
IAEA-N1			2.4	0.1
IAEA-N2			22.6	
IAEA-N2			22.2	
IAEA-N2			22.4	
IAEA-N2			22.4	0.2

3. RESULTS

3.1. $^{13}\text{C}/^{12}\text{C}$ of carbon dioxide in mineral water

Carbon dioxide of commercial mineral waters can vary significantly (Fig. 4). There are two main sources of carbon dioxide as revealed by their different $^{13}\text{C}/^{12}\text{C}$ ratios. The $^{13}\text{C}/^{12}\text{C}$ ratios of carbon dioxide from wells range between -4 to -8‰ vs. PDB ('well carbon dioxide'). The wells are mainly supplied with CO_2 by recent volcanic activity in the Eifel and Black Forest region. The second group of data between -26 and -44‰ represents carbon dioxide mainly manufactured by burning coal or biomass ('processed carbon dioxide'). This carbon source is dominated by plants using the C_3 photosynthesis pathway, the most common type in plants of our area. German mineral water regulations allow a specific qualification of the mineral water ('carbon dioxide of its own well') to be used on the label only when the carbon dioxide originates exclusively from its own well. Usually customers honor this by paying a higher price. The notion behind the declaration suggests that the mineral water in question is a pure natural product. Processed carbon dioxide may not differ in terms of quality but the mineral water is not received as an entirely natural product. The regulation is unique in Europe.

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