Three combustion reactions in a single EA/IRMS acquisition as a strategy to save helium and energy

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Abstract

RATIONALE: Helium (He) is used in cutting-edge research in industry and science as a carrier and/or ionization gas. The global He shortages have dramatically increased its prices and reduced its availability, to what comes together the current energy crisis. A strategy is proposed to save He and energy in elemental analysis/isotope ratio mass spectrometry (EA/IRMS). METHODS: A method for analysis of carbon and nitrogen isotope composition (δ^{13}C and δ^{15}N values) is proposed using two or three sequential combustion reactions in a single EA/IRMS acquisition. The methods (hereafter called 2×EA/IRMS and 3×EA/IRMS) use the time needed for the peak center and reference gas (CO_2 or N_2) pulses to measure δ^{13}C or δ^{15}N in two or three capsules with samples or standards. The combustion cycles can be replicate analyses of the same or different material. RESULTS: The methods were validated with replicate analysis of C and N in RMs and laboratory standards of a broad range of biological and geological matrices, δ^{13}C and δ^{15}N values, and C/N molar ratios. The accuracy and precision of the 2×EA/IRMS and 3×EA/IRMS values were15 essentially the same, with good agreement between the mean ± 1 SD values from RMs and standard analyses and the recommended or accepted values and their uncertainties. CONCLUSIONS: The proposed methods save He, save energy, save reference gases (CO_2, N_2), and O_2, while reducing the analysis and instrumental times by ca. 50 %.

Rapid communications in Mass Spectrometry

LETTER TO THE EDITOR

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The global energy shortage crisis, helium (He) shortages and rising prices worldwide have forced academic institutions and industries to reduce their consumption and look for alternatives[1]. The excessive He consumption and operating time of continuous He-flow instruments using high-temperature combustion or pyrolysis reactors linked to isotope ratio mass spectrometers further complicate this problem. Such challenges should be addressed. The stable isotope ratios of carbon (δ^{13}C relative to Vienna Pee Dee Belemnite limestone), nitrogen (δ^{15}N relative to molecular nitrogen in air) and sulfur (δ^{34}S relative to Vienna Cañon Diablo Troilite) in bulk samples determined by elemental analysis and isotope ratio mass spectrometry (EA/IRMS) have been proven to be a remarkable tool to investigate processes in biogeochemical and geochemical cycles. For δ^{34}S measurements, an alternative instrumental approach, operating with less He than EA/IRMS, is multicollector inductively coupled plasma/mass spectrometry (i.e., with He-Ar or Ar alone as the aerosol carrier)[2]. However, to date, there is no alternative to bypass EA/IRMS for the analysis of C and N isotopes. A large number of EA/IRMS δ^{13}C and δ^{15}N measurements with high He consumption are routinely being used in a wide range of research and industrial applications in fields including geochemistry, biology, pharmacy, medicine, food control, food authentication, archaeometry, and forensic sciences. Most He is recovered as a byproduct from natural gas accumulations, and the conventional reserves are becoming scarce or logistically unavailable, raising concerns about He shortages and price increases in the scientific research community[3,4].

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While replacing fossil fuels with alternative or renewable energy may be a way to realize sustainable power sources,[5] managing the He supply will be more challenging. He used as carrier gas in gas chromatography (GC) methods can be replaced with H_2 when using flame ionization detection (GC/FID) or with N_2 in some GC/MS assays. Replacing He with another gas (i.e., H_2, N_2, O_2) in EA/IRMS or TC-EA/IRMS would be impossible because the gas could be the analyte and otherwise would provide a high background signal. Here, I present a strategy to cope with He shortages in EA/IRMS.

Not all industrial or academic applications require both C and N isotopes, and the material to be analyzed may contain very little N (e.g., lipids, carbohydrates, hydrocarbons, most geological materials), which makes methods analyzing $\delta^{13}C$ and $\delta^{15}N$ in the same acquisition unsuitable. Previously, I published a method for analyzing liquid samples (e.g., ethanol, wine) containing volatile analytes using two sample-capsule combustion reactions in a single EA/IRMS acquisition[6]. This procedure was shown to reduce the time of stay of the liquid-containing tin capsule remained in the cavity of the autosampler on the sampler slide, thus reducing its residence time in the autosampler drum and the risk of sample loss by evaporation. This optimized EA/IRMS method was only used to analyze C-rich samples with very low N content. Three 20 s pulses of CO_2 reference gas with a known $\delta^{13}C$ value were followed by the CO_2 peaks resulting from two successive EA combustion reactions. In this method (hereafter called 2×EA/IRMS), the time required to reach the CO_2 peak center and inject the reference gas pulses is used to measure the $^{13}C/^{12}C$ ratio of the CO_2 produced by two samples or calibration standards. Here, improvements of the 2×EA/IRMS method for both C and N isotope analysis are presented, then extended to include three EA combustion reactions (i.e., 3×EA/IRMS method), and finally validated with a set of international reference materials (RMs) of different matrices and covering a broad range of $\delta^{13}C$ and $\delta^{15}N$ values and C/N molar ratios (Table 1). This contribution will help overcome difficulties in the supply of He tanks, energy shortages, and dramatic increase in the prices of He bottles and energy.

Here, modifications of the EA conditions and acquisition methods previously presented in Spangenberg and Zufferey[6] are adopted. The system consisted of a Carlo Erba 1108 elemental analyzer fitted with an AS-200LS pneumatic autosampler with a 49-sample drum (Fisons Instruments, Milan, Italy) and a ConFlo III continuous flow open-split interface linked to a Delta V Plus isotope ratio mass spectrometer (Thermo Fisher Scientific, Bremen, Germany). Aliquots of calibration standards and RMs were weighed in tin capsules. They were combusted at 1020 °C in a quartz reactor (450 mm × 18 mm i.d., 2 mm wall) filled in house with 40 mm quartz wool, followed by 60 mm of silvered cobaltous/cobaltic oxide (Ag-Co_3O_4), 10 mm quartz wool, 120 mm chromium oxide (Cr_2O_3), and 5 mm quartz wool at the top. EA sonsumables fwere obtained rom Säntis Analytical, Teufen, Switzerland. At the time of the combustion, a 60 s O_2 pulse (30 mL min^{-1}) was introduced into the He carrier flow of 60 mL min^{-1}, which is a significantly lower flow rate than the conventionally used rate of 80 mL min^{-1}. A quartz insert (210 mm × 13 mm i.d., wall 2 mm, with 5 mm quartz wool at the bottom) was used to collect the ash and residues from the tin capsules and replaced after 100–150 combustion reactions. The reactor packing could generally be used for the combustion of 800–1200 samples. The combustion-produced gases (i.e., CO_2, N_2, NO_x and H_2O) were carried by the He through a reduction reactor—filled from bottom upward with 40 mm quartz wool, 50 mm copper oxide (CuO), 280 mm copper grains, 10 mm quartz wool, 50 mm copper oxide, and 10 mm quartz wool at the top—at 640 °C to remove excess O_2 and reduce nonstoichiometric nitrous products to N_2. The gases were then carried through a glass column (110 m × 12 mm i.d., 2 mm wall) filled with anhydrous magnesium perchlorate ($Mg(ClO_4)_2$) to remove water. The dried N_2 and CO_2 were separated in a chromatographic column (3 m × 4 mm i.d. stainless steel column packed with Porapak® QS 50/80 mesh) at 80 °C, and carried into the source of the mass spectrometer for measurement of the isotope ratios of C and N. The GC device was heated 10 °C higher than the routinely used value of 70 °C (IDYST, University of Lausanne), to improve the separation of the N_2 and CO_2 peaks with the shortest possible retention times after reducing the He carrier flow. Separate EA/IRMS analytical sequences with optimized sample aliquot sizes (depending on the C/N ratio of the sample) were used for the determination of $\delta^{13}C$ and $\delta^{15}N$ values. The $^{15}N/^{14}N$ ratios were measured in CO_2-free gas, obtained by connecting a column (110 m × 12 mm i.d., 2 mm wall) filled with soda lime before the water trap. Three reference gas (N_2 or CO_2, both [?]99.999 purity) pulses were injected into

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the He carrier gas before the sample peak eluted from the gas chromatograph. The 3xEA/IRMS methods for C- and N-isotope analysis were essentially the same; the conditions after the peak center included three activations of the elemental analyzer (at 45–50 s, 280–285 s, and 515–520 s), no He-dilution, three reference gas pulses (at 20–40 s, 70–90 s, and 120–140 s), and an acquisition end time of 900 s. The 2xEA/IRMS method had only the first two activations of the elemental analyzer and an acquisition end time of 700 s (Figure 1). Sample aliquot sizes were optimized to obtain signals with the integrated peak area (total area in Vs) of the major isotopes (m /z 44, 45, and 46 for CO_2 and m /z 28, 29, and 30 for N_2) within +-30 % of the total area of the reference gas peaks. Isotopic data were acquired and processed using ISODAT 3.0 software (Thermo Fischer Scientific). The sample peaks were evaluated by assigning a δ -value to the second reference peak. Normalization of the measured raw δ -values to the international isotope reference scale, VPDB-LSVEC lithium carbonate (hereafter VPDB) for C and air-N_2 for N, was performed by 3-point linear calibrations with certified RMs and well-calibrated in-house standards. The samples and calibration standards were weighed in 3.3 × 5 mm tin capsules. The analytical sequences consisted of two sets of three calibration standards measured in duplicate with the 2×EA/IRMS method at the beginning and end of each run, with typically 40 to 60 sample capsules measured with the 2×EA/IRMS or 3×EA/IRMS method between the calibration standards. The tin capsules combusted in the same adquision conatined aliquots odf the same or different sample or standard. The autosampler needed to be refilled during the runs. The δ -values were reported using the milliurey (mUr) —a synonym of the no longe acceptable unit per mil (of Units.[7]

The validation of the developed procedures (2×EA/IRMS and 3×EA/IRMS) was based on replicate ($n = 4$–6) C and N isotope analysis of RMs and laboratory standards performed during eight analytical sessions (August-September 2023). The results are reported in Table 1 as the mean ± 1 standard deviation (SD). The RMs and laboratory standards covered a wide range of δ ^{13}C values from –43.69 to –0.67 mUr ($n =$17) and δ ^{15}N values between –4.52 and 50.137 mUr ($n =$8). The accuracy of the proposed procedures was assessed by the agreement between the measured and the accepted/recommended isotope δ -values. The differences between the 3×EA/IRMS values and the accepted δ ^{13}C values (0.04 ± 0.07 mUr) were similar to those for 2×EA/IRMS (0.01 ± 0.07 mUr). The highest differences were for the NBS22 Oil RM. Similar results were obtained for δ^{15}N, with the differences between the 3×EA/IRMS values and the accepted values (–0.02 ± 0.11 mUr) comparable to those between the 2×EA/IRMS values and the accepted values (–0.02 ± 0.10 mUr). The average precision (1 SD values) of the 2×EA/IRMS and 3×EA/IRMS values was essentially the same (0.06 ± 0.03 mUr and 0.06 ± 0.02 mUr for δ ^{13}C; 0.09 ± 0.03 mUr and 0.09 ± 0.05 mUr for the δ ^{15}N). The reproducibility values, estimated from the SD values, are within the range of the uncertainties of accepted values for RMs and laboratory standards (Table 1). Finally, the proposed procedures were validated with unknown samples from leaves, stems, and roots of C_3 and C_4 plants (i.e., grapevine and corn) and decarbonated soil fractions. The mean of the δ ^{13}C and δ ^{15}N values from the 2×EA/IRMS and 3×EA/IRMS analyses ($n = 5$) are in good agreement with the values obtained by conventional EA/IRMS ($n = 4$), with analytical errors of ±0.05 for δ ^{13}C and ±0.10 for δ ^{15}N.

In summary, the proposed adaptation of the routinely used EA/IRMS method significantly reduces the He carrier consumption and analysis time per sample by adding second and third combustion cycles. The conventional 600 mL He consumption and 600 s instrument time become 350 mL He and 300 s (2×EA/IRMS) or 300 s and 300 mL He and 300 s (3×EA/IRMS). The accuracy and precision of the δ ^{13}C and δ ^{15}N values remain unaffected. Both methods save He, save energy, save reference gases (CO_2, N_2), and O_2, while reducing the analysis and instrumental times by ca. 50 %. In conclusion, the approach described here is particularly suitable for academia or industry and research, where cost-effective high throughput and accurate and precise replicate analysis of C and/or N isotopes is needed. Additionally, the method benefits students and researchers by reducing the turnaround time and providing significant cost savings to the laboratory in terms of helium and energy.

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CAPTIONS

Table 1. Results obtained by 2×EA/IRMS and 3×EA/IRMS measurements of international reference materials and laboratory standards.[a]

[a] n.a. = not applicable; n.d. = not determined

Figure 1. Typical 3×EA/IRMS chromatogram for carbon (A) and nitrogen (B) isotope analysis. The traces of m/z 44, 45, and 46 and of m/z 28, 29, and 30 represent ions of the CO_2 and N_2 reference gases (three rectangular peaks) followed by peaks from three consecutive combusiton reactions of tin capsules containing aliquots of the same or different sample or standard. The traces of the m/z ratios 45/44 and 46/44 show the contribution of N_2 to the background (A).

Hosted file

Table-1_Spangenberg_2023_nxEA-IRMS.docx available at https://authorea.com/users/664449/articles/666155-three-combustion-reactions-in-a-single-ea-irms-acquisition-as-a-strategy-to-save-helium-and-energy

A

B

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